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DEVELOPMENT OF SILICONE RUBBERS FOR USE AT TEMPERATURES DOWN TO -100°F.

U. S. GOVERNMENT CONTRACT DA-44-109-QM-64

PROGRESS REPORT

FOR THE PERIOD

DECEMBER 5, 1951 to JUNE 4, 1952

REPORT No. 12

CONNECTICUT HARD RUBBER COMPANY

NEW HAVEN, CONNECTICUT

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SUMMARY OF RESULTS

1. Several new materials were evaluated as reinforcing pigments for General Electric SE-76 silicone rubber with no outstanding results. Celite 318, a diatomaceous earth, and Perlite, an exploded lava, showed poor reinforcement alone.

2. A calcined aluminum silicate, Burgess Iceberg Pigment, is moderately effective at higher loadings, giving a soft stock of 400 p.s.i. tensile strength.

3. A fine form of magnesium trisilicate was found to inhibit peroxide curing due to its high basicity.

4. A fine grade of clay known as Whitetex was supplied with a claim of high reinforcement in silicone rubber. We found a maximum tensile strength of only 400 p.s.i. This material would, however, be a good extender for silicone stocks.

5. A finely-divided graphitic mica, known as Micalith G, gave a cured silicone rubber of rather low strength but of a leathery nature. This interesting property is believed to be due to its fine plate-like crystal structure. Micalith is reputed to impart excellent electrical properties to silicone resins.

6. Several new forms of silica pigments were evaluated. Si-O-Lite, an inexpensive by-product silica, was found to be a moderately good pigment giving up to 450 p.s.i. tensile strength with SE-76 gum. Two additional forms of Hi-Sil, a fine silica produced by

Columbia-Southern Chemical Co., were found to have better reinforcing properties than the original Hi-Sil C. A special fine grind called Hi-Sil CVX2 gave up to 500 p.s.i. tensile strength, while another form known as Hi-Sil 52-WHB-42 gave over 750 p.s.i. tensile strength at 20 volume loading. This places it in a class with Santocel C as one of the best reinforcing pigments, and it is said to be considerably less expensive.

7. Additional samples of 0.05 micron rutile and anatase titanium dioxides whose pH varied from 3.8 to 8.1 caused benzoyl peroxide decomposition and loss of cure at low volume loadings. Cures could be obtained at 10 volume loading but they did not give outstanding physical properties.

8. DuPont GS199S Silica has been found to possess curing properties of its own in addition to its reinforcing properties. The silica causes slower cures than benzoyl peroxide, but the curing effect persists at temperatures of 300 to 480°F. resulting in high temperature brittleness.

9. The physical properties obtainable with SE-76 were found to depend strongly on slight variations in its viscosity. This effect is more noticeable with the GS Silica curing system than with peroxide, and very high tensile GS Silica stocks cannot be made with a soft gum. The variation in SE-76 may be due to its degree of polymerization and the consequent change in its average molecular weight. It is believed that a drop in average molecular

weight from about 250,000 to about 175,000 is responsible for the observed decrease in maximum tensile strength of 1800 to 700 p.s.i. with GS Silica.

10. General Electric SE-76 gum gives only 25 p.s.i. tensile strength when cured with benzoyl peroxide in the absence of reinforcing fillers. The best available reinforcing fillers, other than GS 199S Silica, without chemical cross-linking agents (i.e. peroxide) give up to 250 p.s.i. tensile strength and 300 per cent elongation.

11. A dispersion of benzoyl peroxide in silicone oil is no more and no less effective than dry benzoyl peroxide powder in mixing with and curing SE-76 gum.

12. Coating three of the better reinforcing fillers, Titanox RANC, Santocel C and Hi-Sil with 0.2 - 100 per cent by weight of a low molecular weight silicone oil improves their mixing and wettability with silicone gum. At optimum compounding conditions, tensile strength and elongation increases of over 50 per cent were obtained. However, at higher temperatures of curing, the oil coating volatilized off and the stocks became shorter and harder than the uncoated control sample. A higher molecular weight coating oil should improve this situation.

13. Preliminary analysis showed that curing pigments such as GS 199S Silica contain organic constituents on the surface which are removable by distillation in air as lower alcohols. To

determine whether the active coating could be merely absorbed alcohol on the pigment surface, two silica reinforcing fillers were coated with alcohols and hydrocarbons by physical absorption from the vapor phase. Tert-amyl alcohol and iso-amyl alcohol at 2 - 5 per cent coating induced slight additional reinforcing properties to Santocel C and Hi-Sil silicas in the absence of peroxide, while n-octane did not.

14. A large number of stocks were compounded to evaluate the properties and action of DuPont GS 199S Silica as a simultaneous curing and reinforcing pigment for silicone rubber. In the absence of benzoyl peroxide, stocks of 1800 p.s.i. tensile strength and 800 per cent elongation at 64 Shore A hardness were produced with SE-76 gum. With a small amount of peroxide, tensile strength was raised to 1900 p.s.i. and elongation to 850 per cent at 73 Shore A hardness. To our best knowledge these represent the highest degree of reinforcement ever attained in silicone rubber.

15. GS Silica may be milled into SE-76 gum up to 52 volume per cent loading, due to the increased wettability and plasticizing action resulting from its organic coating. The best rubber stocks are obtained between 15 and 25 volume loading, depending on the viscosity of gum used. Curing by the GS Silica alone will take place at 10 volumes and above. At maximum loading of 50 volumes, a hard semi-flexible resinous material of good dielectric properties is obtained.

16. The optimum vulcanizing and reinforcing properties of GS Silica are obtained with cures at 300 to 350°F. At this temperature the stocks are relatively stable. Extended curing at 400°F. causes scorching, with increasing hardness, while at 480°F. the stock becomes brittle in a few hours. Low temperature properties of the stocks are good with brittle points below -80°F. GS Silica stocks are thus limited at present in their temperature serviceability. However, it will probably be possible to correct this important disadvantage.

17. The properties of GS Silica-cured stocks are more sensitive to variations in the silicone gum than ordinary peroxide-cured recipes. A drop of over one-half in tensile strength occurred with a new batch of SE-76 of slightly lower viscosity. There will be a need for closer control on the raw silicone polymer for use with GS Silica.

18. Banbury mixes of GS Silica made by DuPont were unsatisfactory, due to heat build-up and premature curing during mixing.

19. Milling difficulties due to the electrostatic charge and high fly loss of GS Silica may be effectively controlled with a very humid atmosphere in the vicinity of the mill rolls.

20. A sample of GS Silica, purposely densified for ease in handling, did not yield quite as good properties as the original highly dispersed samples. Agglomerated GS Silica particles apparently do not break down entirely during milling, as is known to occur with densified carbon blacks.

21. GS Silica will cure recipes containing other reinforcing fillers or extenders. Of several tested, Celite Superfloss was the best material for extender use with GS. Pigmenting fillers, such as titanium dioxide or carbon black, may be added to GS stocks in sufficient quantity to color them without affecting the properties.

22. GS Silica master batch stocks were shelf-aged for 60 days at 80°F. and 21 days at 125°F. before curing without significant change in the cured properties.

23. Our analysis of GS 199S Silica shows that it is an extremely finely divided porous silica of approximately 0.01 micron particle size. It contains 15 per cent by weight of an organic coating, which may be removed by dissolving the silica with strong alkali and proves to be n-butyl alcohol. The coating cannot be solvent extracted and is chemically bound to the silica gel structure in the form of butyl silicate. These surface butoxy groups render the silica hydrophobic and organophilic. At 200°F. in air the butoxy groups begin to split off.

24. Some alkoxy-substituted silicas were prepared in our laboratory which were similar in composition to GS 199S. One preparation showed definite curing activity when heated with SE-76.

25. A silicone rubber V-belt and tire tread stock, fabricated from high tensile GS Silica stock, operated satisfactorily in initial tests as a hydrocarbon rubber substitute for low temperature application.

INTRODUCTION

Report No.10 covering the quarter ending December 4, 1951 gave preliminary results on the use of Du Pont Silica GS199S in General Electric silicone rubber SE-76.

Report No.11 which was released June 5, 1952 contained a summary and conclusions drawn from work done on the swelling of silicone rubber in various solvents leading to determination of the theoretical important quantities M_c, molecular weight between cross-links; δ, cohesive energy density; and μ the solvent-polymer interaction coefficient.

Progress Report No.12 covers the period from December 5, 1951 to June 4, 1952. In this report data on additional new pigments which have been tried in silicone rubber are reported. The coating of certain pigments with silicone oils and with other organic coatings is discussed. The analysis of Du Pont GS199S Silica is included as well as very extensive compounding trials of GS199S Silica in SE-76 silicone rubber.

In this report is reported for the first time our observation that silicone rubber can be simultaneously reinforced and vulcanized by a single material. The outstanding example of this is Du Pont GS199S Silica.

A thorough study of the effects of this pigment in all concentrations under all curing conditions as well as in the presence of other reinforcing pigments is included. Patent protection covering simultaneous reinforcement and vulcanizing action is being sought as a result of the work reported herein. The program of the Grasselli Chemical Division of the Du Pont Company has been modified with the intent of producing a further improved type of GS Silica.

It was learned in the course of GS Silica work that securing maximum tensile and elongation results depends not only on the method and preparation of the pigment, but also on the type of SE-76 rubber that is used. Because of lack of control over the specifications of the SE-76 rubber, it is impossible at this time for us to state exactly what these specifications should be. Superior results have generally been obtained with firmer, less fluid and presumably higher molecular weight varieties of the rubber. A more complete analysis of this problem should be possible in the succeeding Report No.13.

By reviewing the past progress on the reinforcement of silicone rubber, it has been possible to write a paper entitled "The Compounding of Silicone Rubber II" which will be read at the meeting of the Rubber Division of the American Chemical Society October 29,30,31,1952. The authors of the paper are W.B. Spencer, W.B. Davis, F. L. Kilbourne Jr. of The Connecticut Hard Rubber Company and J.C.Montermoso of the Office of the Quartermaster General.

Although the final specifications of neither the pigment or the silicone rubber necessary to produce the highest type of compounded silicone rubber are yet fixed, attempts have been made outside of this contract to make practical use of some of these developments. GS Silica compounds were used to construct silicone fan belts which exceeded the quality of any made previously. A camel-back material for retreading tires was also compounded using the GS Silica in SE-76 rubber and successfully applied as a retread on a tire. Tread wear measured after a few hundred miles was not excessive. In order to promote a more rapid development of practical use of these and other compounding developments in silicones and other specialty purpose rubbers, a new contract has been entered into between The Connecticut Hard Rubber Company and the Office of the Quartermaster General in which special end items will be worked on with these improved compounding techniques.

EXPERIMENTAL PART

I. REINFORCEMENT OF SILICONE RUBBER

A. New Pigments in General Electric SE-76 Silicone Gum.

1. Celite 318

Celite 318 is a diatomaceous earth pigment supplied by the Johns-Manville Corporation. It is a fine diatomaceous earth of the Superfloss grade but coated with aluminum stearate to improve wetting properties. Table I-A-1 gives the physical test results with this pigment in SE-76 gum at 20 to 80 per cent by weight loading with 2 per cent benzoyl peroxide as the curing agent. Maximum physical properties with Celite 318 occurred at 40 weight per cent loading. This pigment is not a good reinforcing pigment, however, since only 218 p.s.i. tensile strength and 16 hardness were obtained with this recipe. Celite 318 might prove effective as a cheap additive to better silica stocks such as Santocel C.

2. Perlite

Perlite is an exploded lava. It is light and fluffy and used for introducing porosity in building materials. It was evaluated both as a pigment and extender in silicone rubber stocks. Data in Table I-A-2 show that Perlite is not a reinforcing pigment by itself. When it was used as an extender for General Electric 81223 stock (a Santocel C reinforced stock) 25 per cent by weight lowered the tensile

TABLE I-A-1

Evaluation of Celite 318

Compound No.	Wt. % of Pigment	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elongation Per cent	Hardness Shore A
2103	20	59	118	126	525	13
2103-1	30	59	132	206	850	15
2103-2	40	75	143	218	1050	16
2103-3	80	58	73	73	625	20

The stocks were compounded with SE-76 silicone gum.
The press cure was 15 minutes at 230°F.
The oven cure was 1 hour at 300°F.
Two per cent benzoyl peroxide was used as a curing agent.

TABLE I-A-2

Perlite as a Pigment and Extender

Compound No.	Compounded with	Wt. % of Perlite	Oven Cure	Tensile Strength p.s.i.	Elongation Per cent	Hardness Shore A
2156-1	SE-76 alone	20	1 hr. @ 300°F.	56	88	28
			1 hr. @ 400°F.	44	88	30
Control	81223 stock	0	1 hr. @ 300°F.	865	275	50
2156-3	81223 stock	25	1 hr. @ 300°F.	544	100	63
			1 hr. @ 400°F.	547	88	63

The press cure was 15 minutes at 230°F.
Two per cent benzoyl peroxide was used with the SE-76 but no additional peroxide was added to the 81223.

strength about 37 per cent and the elongation about 200 per cent, indicating that it is not a very effective material for this purpose. This is probably due to its large particle size and its fused non-porous composition.

3. Burgess Iceberg Pigment

Another new pigment obtained for evaluation in silicone rubber was Burgess Iceberg Pigment. It is a calcined aluminum silicate. Data in Table I-A-3 show that this pigment could be incorporated up to 80 per cent by weight into SE-76 but that its reinforcing properties are evident only at high loadings. At 80 weight per cent, the tensile strength of 382 p.s.i. indicates a fair degree of reinforcement. This 80 per cent stock is still not very hard, however, and more pigment could probably be incorporated if desired.

4. Micalith G

Micalith G is a finely divided (325 mesh) graphitic mica with a carbon content of about 0.5 per cent. This material is supplied by General Mining Associates and is reported to impart excellent electrical properties to silicone resins. Of particular interest is its unusual crystal structure. Each particle is composed of many thin platelets which cleave under stress as does ordinary mica. We were interested in learning whether this shape had any effect on reinforcement. Table I-A-4 gives data for 10 to 50 volumes of Micalith G in SE-76 using benzoyl peroxide for the cure. Reinforcement with this pigment

TABLE I-A-3

Evaluation of Burgess Iceberg Pigment

Compound No.	Wt. % of Pigment	St.@ 100%	Tensile Strength p.s.i.	Elongation Per cent	Hardness Shore A
2104	20	43	77	175	20
2104-1	30	44	67	175	20
2104-2	40	64	178	200	25
2104-3	80	144	382	200	35

The stocks were compounded with 81176 silicone gum.
The press cure was 15 minutes at 230°F.
The oven cure was 1 hour at 300°F.
Two per cent benzoyl peroxide was used as a curing agent.

TABLE I-A-4

Evaluation of Micalith G

Compound No.	Vol. % of Pigment	Oven Cure	Tensile Strength p.s.i.	Elongation Per cent	Hardness Shore A
2183-1	10	1 hr. @ 300°F.	100	200	25
	"	16 hrs. @ 400°F.	98	175	23
2183-2	20	1 hr. @ 300°F.		Cracked slab	
	"	16 hrs. @ 400°F.	186	150	30
2183-3	30	1 hr. @ 300°F.	206	187	40
	"	16 hrs. @ 400°F.	282	75	64
2183-4	40	1 hr. @ 300°F.	191	150	43
	"	16 hrs. @ 400°F.	198	25	69
2183-5	50	1 hr. @ 300°F.	173	87	62
	"	16 hrs. @ 400°F.		No Cure	
2183-6	50	1 hr. @ 300°F.	290	75	62
	"	16 hrs. @ 400°F.	443	25	87

The stocks were compounded with SE-76 silicone gum.
The press cure was 15 minutes at 230°F.
Two per cent benzoyl peroxide was used as a curing agent, except in 2183-6 where 4 per cent was used.

is not outstanding, the most rubbery sample having about 200 p.s.i. tensile strength and 190 per cent elongation. The batches with high volume loadings (40 and 50) were, however, interesting in that they were leathery to the touch. We see no immediate use for this type of silicone stock, but its combination of good electrical properties and leathery nature may be useful in some future application. This unusual property is undoubtedly due to the shape of the Mica-lith particles.

5. Si-O-Lite

A sample of Si-O-Lite pigment was obtained by us from Mallinkrodt Chemical Company for evaluation. This is an inexpensive by-product silica of about 1 micron particle size, and this sample had been heated to remove all but four per cent of volatile materials. Compared to the untreated Si-O-Lite, which was evaluated previously and reported in Progress Report #10, the heated Si-O-Lite gave slightly higher tensile strengths at equivalent volume loadings (about 30 per cent higher at 20 and 25 volumes). This is, therefore, the preferred form of Si-O-Lite. This pigment is a moderately good reinforcing pigment and is said to be considerably cheaper than the other types of silica, such as Santocel C. The data are presented in Table I-A-5.

TABLE I-A-5

Evaluation of Si-O-Lite Pigment
(Less than 4.0% loss on ignition)

Compound No.	Volume % of Pigment	St.@ 100%	Tensile Strength p.s.i.	Elongation Per cent	Hardness Shore A
2151-1	15	111	353	238	33
2151-2	20	164	501	238	40
2151-3	25	324	501	163	52
2151-4	40	464	464	100	71

The stocks were compounded with SE-76 silicone gum.
The press cure was 15 minutes at 230°F.
The oven cure was 1 hour at 300°F.
Two per cent benzoyl peroxide was used as a curing agent.

6. <u>Magnesium Trisilicate</u>

A fine form of magnesium trisilicate has also been evaluated. This was obtained from Mallinkrodt and has been used mainly as an anti-acid in pharmaceutical compounds. We compounded this pigment at loadings of 20 to 100 per cent by weight. The data in Table I-A-6 indicate that the trisilicate inhibited curing of silicone gum by peroxide, even at 20 per cent. This is undoubtedly due to its high basicity, and consequent catalytic effect on peroxide decomposition. The material is of little value in silicone rubber compounding.

7. <u>Various Types of Hi-Sil</u>

We have done a considerable amount of compounding with Hi-Sil. This pigment is a hydrated silica of 0.025 micron particle size supplied by the Columbia-Southern Division, Pittsburgh Plate Glass Co. It is a fairly good reinforcing pigment, although it is probably not so porous as Santocel C. We asked the supplier about other forms of this material and were given two others, called Hi-Sil CXV2 and Hi-Sil 52-WHB-42. The CXV2 is a special fine grind of regular Hi-Sil while the 52-WHB-42 is apparently prepared by another process and is more nearly like Santocel C. Table I-A-7 gives data for these Hi-Sil pigments at 10, 15, 20 and 25 volume loadings and compares them with similar data for the

TABLE I-A-6

Evaluation of Magnesium Trisilicate

Compound No.	Wt. % of Pigment	Tensile Strength p.s.i.	Elongation Per cent	Hardness Shore A	Remarks
2155-1	20	152	675	10	Soft and slightly tacky.
2155-2	40	---	---	--	No cure; very soft and pasty.
2155-3	60	---	---	18	Outer surface seemed cured but middle not cured, air pockets, laminated.
2155-4	80	77	75	58	Laminated through center, air pockets smaller and fewer than in 2155-3.
2155-5	100	---	---	89	Very brittle, hard and boardlike. Brown spots over entire strip. A separation of gum from pigment was evident.

The stocks were compounded with SE-76 silicone gum (Batch No. 5946).
The press cure was 15 minutes at 230°F.
Two per cent benzoyl peroxide was used as a curing agent.
The oven cure was 1 hour at 300°F.

TABLE I-A-7

Comparison of Various Types of Hi-Sil Pigment.

Compound No.	Pigment	Volume % of Pigment	St.@ 200%	Tensile Strength p.s.i.	Elongation Per cent	Hardness Shore A
2251	Santocel C	10	222	614	463	45
2245	Hi-Sil C	10	135	284	450	28
2278	Hi-Sil CXV2	10	128	436	613	30
2244	Hi-Sil 52-WHB-42	10	137	344	417	31
2251-1	Santocel C	15	377	780	398	65
2245-1	Hi-Sil C	15	189	392	500	40
2278-1	Hi-Sil CXV2	15	200	500	588	46
2244-1	Hi-Sil 52-WHB-42	15	308	712	363	37
2251-2	Santocel C	20	481	810	325	72
2245-2	Hi-Sil C	20	152	366	587	53
2278-2	Hi-Sil CXV2	20	247	432	400	60
2244-2	Hi-Sil 52-WHB-42	20	482	757	300	42
2278-3	Hi-Sil CXV2	25	373	374	250	72

The stocks were compounded with SE-76 silicone gum (Batch No. 11317-3).
Press cure was 15 minutes at 230°F.
Oven cure was 1 hour at 300°F.
Two per cent benzoyl peroxide was used as a curing agent.

earlier Hi-Sil C and Santocel C. The original Hi-Sil C gave less than half the tensile strength of Santocel C, with about the same or higher elongation. Hi-Sil CXV2 gives tensile strengths about 40 per cent higher than Hi-Sil C and about 50 to 60 per cent of Santocel C, maintaining high elongation. Hi-Sil 52-WHB-42 shows superior reinforcing properties at 15 and 20 volume loadings, where tensile strengths of over 700 p.s.i. were obtained to compare favorably with Santocel C. These later developments in Hi-Sil are definitely superior, and the 52-WHB-42 is very close to Santocel C in reinforcing power.

8. Whitetex

The whitetex pigment is a fine grade of clay.
The data in Table I-A-8 show that up to 80 volumes of this pigment can be incorporated in SE-76 gum, with moderate reinforcing properties in the 30 to 60 volume range. Whitetex was claimed to give 800 p.s.i. tensile strength, but the best we obtained was 400 p.s.i. at 60 volume loading.

9. Fine Titanox MP-561

We obtained additional samples of fine particle size titanium dioxide pigments from National Lead Co. to further study these materials in silicone rubber.

TABLE I-A-8

Evaluation of Whitetex

Compound No.	Vol. % of Pigment	St.@ 100%	Tensile Strength p.s.i.	Elongation Per cent	Hardness Shore A
2260	10	56	124	237	20
2260-1	15	56	196	263	22
2260-2	20	88	263	250	28
2260-3	30	171	410	212	42
2267-1	40	285	393	175	52
2267-2	60	375	390	112	72
2267-3	80	---	310	75	84

The stocks were compounded with SE-76 silicone gum.
The press cure was 15 minutes at 230°F.
The oven cure was 1 hour at 300°F.
Two per cent benzoyl peroxide was used as a curing agent.

Table I-A-9 gives the crystal form and average particle size of these titanium dioxides, together with our compounding results with SE-76 gum. Titanox RANC was evaluated some time ago and found to be a good reinforcing pigment at higher volume loadings. Another form of titanium dioxide, Rayox 110, was also found to be a good reinforcing material. We had thought that smaller particle size titanium dioxides would exhibit stronger reinforcing properties. The data show that this is not necessarily true, with improvements in some cases and none in others. It should be noted that the data in Table I-A-9 is based on 10 volume per cent loading of the five titanias, and that the physical properties of numbers MP-561-5, 8 and 10 compare favorably with those of RANC at this loading. However, RANC will give better reinforcement at higher loadings, while we found that these finer samples could not be incorporated much above 10 volume per cent. This is probably due to their higher surface area, and consequently greater absorption of polymer. They are therefore generally unsatisfactory as pigments.

Comparison of the seven fine titania samples shows that MP-561-5,8 and 10 give good reinforcement. MP-561-5 is a rutile TiO_2 of a very small particle size and high pH(8.1). MP-561-8 and 10 are Anatase form, and of low pH(<3.8). All of these fine titanias were active in

Table I-A-9

Evaluation of Various Grades of Titanium Dioxides
(10 Vol. % of Pigment)

Compound No.	Code No.	Type	Particle Size, micron	pH of Pigment	St. @ 100%	Tensile Strength p.s.i.	Elongation Per cent	Hardness Shore A
2094	MP-561-4	Rutile	0.1-0.5 (irreg.)	4.3	55	55	100	29
2094-1	MP-561-5	"	0.01-0.05(needles)	8.1	85	128	200	27
2094-2	MP-561-6	Anatase	0.1-0.5 (irreg.)	6.9	76	76	100	26
2094-3	MP-561-7	"	0.01-0.05 (round)	7.4		No cure		
2094-4	MP-561-8	"	0.05	<3.8	76	110	175	28
2094-5	MP-561-9	"	0.06	<3.8	58	87	175	25
2094-6	MP-561-10	"	0.06	<3.8	106	131	150	30
1824	Rayox 110 (10 vol.)	Rutile	---	7.1	---	124	300	38
1855	Titanox RANC (10 vol.)	"	---	8.0	---	113	325	34
1857	Titanox RANC (40 vol.)	"	---	8.0	---	587	408	46

The stocks were compounded with SE-76 silicone gum.
The press cure was 15 minutes at 230°F.
The oven cure was 1 hour at 300°F.
Four per cent benzoyl peroxide used as a curing agent, except for 1824 and 1855 where 2 per cent was used.

inhibiting benzoyl peroxide cure, and it was necessary to use 4 per cent of peroxide in the samples shown on Table I-A-9. Their inhibition effect on peroxide curing appeared to be more than just an absorption of the peroxide to render it ineffective, and rather like a catalytic agent in aiding its decomposition. The one sample on which no cure could be obtained, MP-561-7, differs from the others chiefly in its high absorptive capacity. Data of the supplier on oil absorption give a relative index of 61 for MP-561-7, compared with 17 to 30 for the other samples.

B. Control Experiments with SE-76 Gums

1. Control on SE-76 Batches

During the period covered by this report, we obtained a new shipment of SE-76 gum from the General Electric Company. It soon became evident that this gum was not the equivalent of the previous shipment we had been using and on which data of the last two reports were based. A check showed, as we had suspected, that it was of a lower average molecular weight. The General Electric people say that this is a preferred gum, according to a customer survey which they have been making, and they are now supplying this new batch entirely.

This new gum is somewhat softer and therefore easier to mill where large quantities are involved. We checked the molecular weight roughly and found that it was approximately 20 per cent less than the previous gum we had been using.

Table I-B-1 contains evaluation of this new gum (batch 11317-3) together with comparable data obtained with the old batch (B-5946). Data on the new batch heated to 8 per cent weight loss to remove some of the extra low molecular weight silicones is also included. Using Santocel C pigment at 15 volumes and two per cent benzoyl peroxide, the new batch of gum gave superior tensile strength at cures of 300 and 400°F. The hardness was, however, considerably lower due to the softness of the gum. When the new gum was heated to an eight per cent weight loss, driving off some of the low molecular weight silicones, the tensile strength and elongation decreased and the hardness was raised to about that of the old gum. Therefore, the new gum is softer but results in good physical properties in a peroxide curing system.

We found, however, a great difference between the two batches of gum when we cured them with GS199S Silica. Tensile strengths up to 1785 p.s.i. with 850 per cent elongation were obtained with the earlier batch of gum (B5946) but we could not duplicate these with the new gum, where tensile strengths of only 500 to 1000 p.s.i. were obtained.

TABLE I-B-1

Comparison of Two Batches of SE-76 with Santocel C and GS Silica

Compound No.	Recipe	Oven Cure	St.@ 200%	Tensile Strength p.s.i.	Elongation Per cent	Hardness Shore A	Date Compounded
2228-1	SE-76 (B-5946)	1 hr. @ 300°F.	485	835	325	51	6/3/52
	Santocel C	24 hrs. @ 300°F.	580	805	300	56	"
	15 Vols. 2% B.P.	24 hrs. @ 400°F.	520	595	237	50	"
2228	SE-76 (11317-3)	1 hr. @ 300°F.	309	947	425	36	5/22/52
		24 hrs. @ 300°F.	383	775	350	38	"
		24 hrs. @ 400°F.	438	864	325	42	"
2262	SE-76 (11317-3)	1 hr. @ 300°F.	360	664	325	53	6/19/52
	Heated to 8%	24 hrs. @ 400°F.	390	650	312	49	"
	Wt. Loss.						
2229-1	SE-76 (B-5946)	1 hr. @ 300°F.	175	1445	925	62	6/3/52
	GS 199S Silica	24 hrs. @ 300°F.	260	1785	850	66	"
	25 Vols. No. B.P.	24 hrs. @ 400°F.	585	1200	475	80	"
2229	SE-76 (11317-3)	1 hr. @ 300°F.	167	495	837	65	5/22/52
		24 hrs. @ 300°F.	184	690	825	66	"
		24 hrs. @ 400°F.	570	965	425	80	"
2264	SE-76 (11317-3)	1 hr. @ 300°F.	175	235	862	52	6/19/52
	Heated to 8%	24 hrs. @ 300°F.	325	585	837	57	"
	Wt. Loss						

Press cure 15 minutes at 230°F.
SE-76 (11317-3) heated at 300°F. in air to 8% wt. loss.

The heated gum did not perform any better with GS199S, so we could not overcome the difficulty by driving off the lowest molecular weight fraction of the polymer. This fraction is apparently cured satisfactorily by peroxide, but not by GS Silica.

It should be noted that unless otherwise specified, compounds numbered through 2224 were made with SE-76, (batch B-5946) and those from 2225 on were made with SE-76 (batch 11317-3).

2. Curing SE-76 without Pigment

It was of interest to determine the increase in strength of SE-76 gum after it had been cured with benzoyl peroxide but without any reinforcing pigment. This was done with from zero to ten per cent benzoyl peroxide. The data given in Table I-B-2 show that the tensile strength remains essentially constant between two and ten per cent peroxide. Elongation also remained constant and the hardness appeared to reach a maximum with eight per cent. It is probable that the drop in hardness at ten per cent peroxide was due to an excess of benzoic acid by-product which began to override the curing effect by its depolymerizing action.

This experiment again emphasizes the importance of incorporating reinforcing pigments in silicone rubber. Without pigment, silicone rubber has no strength whatsoever, while tensiles of over 1000 p.s.i. can be obtained with the proper pigment.

TABLE I-B-2

SE-76 Cured without pigment

Compound No.	Percent Benzoyl Peroxide	Tensile Strength p. s. i.	Elongation Percent	Hardness Shore A
2188-1	0	No Cure		
2188-2	2	25	25	16
2188-3	4	25	50	21
2188-4	6	25	50	25
2188-5	8	25	50	27
2188-6	10	25	50	23

The press cure was 15 minutes at 230°F.
The oven cure was 1 hour at 300°F.

Since the natural rubber and neoprene possess considerable strength before pigmentation, the pigment is not so critical in these as it is in silicone rubber. Thus, when a proper form of reinforcing pigment is discovered, it should be possible to bring silicone rubber up to the strength of the present hydrocarbon rubbers. G.S.Silica approaches this goal.

3. <u>Santocel C Compounded without Benzoyl Peroxide</u>

Because of our work with GS199S Silica, which is a self-curing pigment, it was of interest to determine what part of this reinforcement might be due to the silica alone. Table I-B-3 gives data for 10 and 15 volumes of Santocel C without any curing agent. At 15 volumes, which is about the maximum amount that can be incorporated, a tensile strength of 185 p.s.i. with 238 per cent elongation and 60 hardness was obtained. Thus, a plain silica pigment will give some reinforcement by itself. However, this does not approach the magnitude of that obtained with GS199S, being about 1/10 of some of our better GS silica stocks.

4. <u>Aerosil Compounded without Benzoyl Peroxide</u>

A similar experiment was performed with 15 volumes of Aerosil pigment. This is a highly porous silica aerogel which reduces to a fine particle size on the mill. It probably has a larger pore volume than Santocel C.

TABLE I-B-3

SANTOCEL C COMPOUNDED WITHOUT BENZOYL PEROXIDE

Compound No.	Volume Loading	Percent Benzoyl Peroxide	Stress at 200 per cent	Tensile Strength p.s.i.	Elongation percent	Hardness Shore A
2152-3	10	None	85	85	225	31
2152-2	10	2.0	342	516	288	46
2152-1	15	None	179	185	238	60
2152-4	15	2.0	514	703	275	67

The stocks were compounded with SE-76 silicone gum
The press cure was 15 minutes at 150°F.
The oven cure was 1 hour at 300°F.

Data in Table I-B-4 show that tensile strengths up to 240 p.s.i. can be obtained with Aerosil without any curing agent. This maximum tensile strength was obtained without any oven cure and it is evident that increasing oven curing is not beneficial to pigment reinforcement by itself. This is undoubtedly due to thermal breakdown of the siloxane polymer at curing temperatures.

5. Luperco AGE Peroxide

A new form of benzoyl peroxide was suggested by the Novadel-Angene Company for evaluation. This is called Luperco AGE peroxide and consists of a paste containing 50 per cent by weight of benzoyl peroxide in a silicone oil. The object here was to obtain better dispersion of peroxide in silicone gum by first dispersing it in oil. Table I-B-5 gives data for this peroxide at one to four per cent with Titanox RANC and Santocel C pigments at their best volume loadings.

The physical properties of compounds cured with this form of benzoyl peroxide are not significantly different from those where dry benzoyl peroxide powder was milled in directly, as is usually done. However, it is interesting to note that the physical properties with Titanox were enhanced more with increased peroxide concentration than those of Santocel C. Reinforcement with Santocel C seems to be less dependent on peroxide concentration in

TABLE I-B-4

AEROSIL COMPOUNDED WITHOUT BENZOYL PEROXIDE

Compound No.	Oven Cure	Stress @ 200 percent	Tensile Strength p. s. i.	Elongation percent	Hardness Shore A
2255	No oven cure	148	240	337	53
2255-A	1 hour @ 300°F.	152	207	300	44
2255-B	24 " @ 300°F.	165	183	250	47
2255-C	1 " @ 400°F.	148	185	262	44
2255-D	8 " @ 480°F.	-	139	188	46

The stocks were compounded with SE-76 silicone gum
The press cure was 15 minutes at 230°F.
Sample 2255 was aged one week after press cure.
The volume loading of Aerosil was 15 throughout.

TABLE I-B-5

Curing Santocel C and Titanox RANC stocks with Luperco AGE Peroxide

Compound No.	Pigment	Percent Peroxide by weight	Stress @ 100 per cent	Tensile Strength p.s.i.	Elongation per cent	Hardness Shore A
2105	Titanox RANC 40 Vol.	1.0	56	448	413	30
2105-1		2.0	206	665	275	45
2105-2		3.0	250	662	200	47
2105-3		4.0	320	695	175	52
2106	Santocel C 20 Vol.	1.0	268	415	213	67
2106-1		2.0	374	648	200	69
2106-2		3.0	431	625	150	75
2106-3		4.0	382	645	200	72

The stocks were compounded with SE-76 silicone gum.
The press cure was 15 minutes at 230°F.
The oven cure was 1 hour at 300°F.
Luperco AGE is a compounded paste containing 50 percent by weight benzoyl peroxide in a silicone oil. The values in this table represent weight percent of the peroxide content alone.

this range. This indicates that Titanox RANC tends to neutralize part of the benzoyl peroxide, producing a deficiency at low concentrations.

C. Compounding Silicone Rubber with Treated Pigments

1. Titanox RANC Coated with Silicone Oil

We have carried out more work with coated pigments. The object of this work was improvement of the pigment-rubber bonds to give greater reinforcement.

Titanox RANC pigment was coated with 0.2 to 10 per cent G.E. silicone oil 9981LT-4, a low viscosity oil. Data are given in Table I-C-1 for this pigment in SE-76 stocks, cured with two per cent benzoyl peroxide (based on total of silicone oil and silicone rubber in the compound).

Using compound #2109 for a control, it appears that a silicone oil coating on the pigment is beneficial to the tensile strength of the cured compound at all concentrations.

The best properties were obtained with five per cent oil on the pigment, where increases of 40 per cent in tensile strength and 35 per cent in elongation were observed, with hardness remaining the same.

With the 300°F. cures, the elongation increased up to 70 per cent over the uncoated Titanox. With cures at 480°F. the tensile strengths did not increase as much and the elongations remained essentially the same as the silicone oil coating was increased. This is probably due to volatilization of the oil at this high curing temperature.

TABLE I-C-1

Titanox R.A.N.C. coated with 9981LT-4 Silicone oil

Compound No.	Weight percent Oil on Pigment	Oven Cure	Stress @ 100 percent	Tensile Strength p.s.i.	Elongation percent	Hardness Shore A
2109	0.0	1 hr. @ 300°F.	213	420	175	47
	"	16 hrs. @ 480°F.	226	309	125	48
2110	0.2	1 hr. @ 300°F.	236	583	212	49
	"	16 hrs. @ 480°F.	253	430	137	49
2111	0.5	1 hr. @ 300°F.	226	407	175	51
	"	16 hrs. @ 480°F.	254	354	125	53
2112	1.0	1 hr. @ 300°F.	298	548	200	50
	"	16 hrs. @ 480°F.	312	376	125	52
2113	2.0	1 hr. @ 300°F.	231	478	187	49
	"	16 hrs. @ 480°F.	320	341	112	51
2114	5.0	1 hr. @ 300°F.	216	608	250	47
	"	16 hrs. @ 480°F.	273	429	137	49
2115	10.0	1 hr. @ 300°F.	177	533	287	40
	"	16 hrs. @ 480°F.	212	410	125	44

The stocks were compounded with SE-76 silicone gum.
The press cure was 15 minutes at 230°F.
2 per cent benzoyl peroxide was used as a curing agent, based on total silicone present.
VOLUME loading 40 per cent based on pigment alone.

Titanox RANC is a good wetting pigment for silicone gum, and soft stocks are usually obtained. It was therefore interesting that incorporation of silicone oil as a coating on the pigment did improve the properties in this manner.

2. Santocel C Coated with Silicone Oil

A similar set of samples was prepared using Santocel C pigment and from 1 to 100 per cent by weight 9981LT-4 as a coating on the pigment. This pigment is, of course, very porous as compared to Titanox and so more oil was required.

Definite improvements in tensile strength by this treatment of Santocel C are observed in the data of Table I-C-2. The maximum effect with a 300°F. cure seems to come at ten per cent of oil, where an increase of 65 per cent in tensile was observed. The tensile strength remains high up to 80 weight per cent of oil and then drops off at 100 per cent. The elongation increases almost continuously as the amount of silicone oil is increased, while the hardness decreases from 70 to 43 with the biggest drop occurring beyond 40 per cent of oil. With a 480°F. cure, the improvement in physical properties is less but still definite, with an optimum occurring at 40 per cent coating. Since Santocel C is a very porous pigment and is wet by silicone gum very well, addition of the oil would be

TABLE I-C-2

SANTOCEL C COATED WITH 9981LT-4 Silicone Oil

Compound No.	Weight percent Oil on Pigment	Oven Cure	Stress @ 100 percent	Tensile Strength p. s. i.	Elongation percent	Hardness Shore A
2116	1	1 hr. @ 300°F.	297	648	250	70
	"	16 hrs.@ 480°F.	403	540	150	74
2118	10	1 hr. @ 300°F.	229	1000	400	63
	"	16 hrs.@ 480°F.	413	488	150	72
2119	20	1 hr. @ 300°F.	259	976	325	66
	"	16 hrs.@ 480°F.	459	560	125	76
2120	40	1 hr. @ 300°F.	234	902	350	62
	"	16 hrs.@ 480°F.	413	716	200	73
2121	60	1 hr. @ 300°F.	189	757	350	50
	"	16 hrs.@ 480°F.	334	680	225	66
2122	80	1 hr. @ 300°F.	162	838	450	47
	"	16 hrs.@ 480°F.	292	541	200	60
2123	100	1 hr. @ 300°F.	117	656	525	43
	"	16 hrs.@ 480°F.	260	614	288	61

The stocks were compounded with SE-76 silicone gum.
The press cure was 15 minutes at 230°F.
2 percent benzoyl peroxide was used as a curing agent, based on total silicone present
Volume loading 20 percent based on pigment alone.

expected to reduce the tightness of the rubber-pigment bond. This is illustrated in the gradual increase in elongation from 250 to 525 per cent and the corresponding reduction in stiffness as the amount of silicone oil on the pigment is increased.

3. <u>Hi-Sil Coated with Silicone Oil</u>

Hi-Sil was coated in a similar manner as shown in Table I-C-3, with up to 60 per cent of 9981LT-4 oil. With curing at 300°F. the tensile strength was 25 per cent higher with about 4.7 per cent coating, but remained essentially constant at about 400 to 460 per cent as the coating was further increased.

With 480°F. cures, the control sample had a tensile strength of only 101 p.s.i., while the oil-coated pigments gave between 213 and 309 p.s.i. Improvements by coating Hi-Sil therefore appeared to be in the same direction but to a lesser degree than those of Santocel C. The exceptional stiffness and hardness of compounds 2129 and 2130 cannot be accounted for.

4. <u>Celite 800 Coated with Vinyl Trichlorosilane</u>

A sample of Celite 800, coated with vinyltrichlorosilane by the Linde Air Products Corporation was tested at 10, 20 and 30 volume loadings. Data in Table I-C-4 give the compounding results, compared with the uncoated Celite 800 at these loadings.

The vinyltrichlorosilane on these samples was completely hydrolyzed, as was the case with those we had prepared

TABLE I-C-3

Hi-Sil coated with 9981LT-4 Silicone Oil

Compound No.	Weight percent Oil on Pigment	Oven Cure	Stress @ 100 percent	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
2124	0	1 hr. @ 300°F.	218	410	175	54
	"	16 hrs.@ 480°F.	95	101	125	41
2125	4.7	1 hr. @ 300°F.	239	503	225	55
	"	16 hrs.@ 480°F.	170	309	237	47
2126	9.7	1 hr. @ 300°F.	184	394	175	48
	"	16 hrs.@ 480°F.	150	225	175	41
2127	23.3	1 hr. @ 300°F.	208	464	200	48
	"	16 hrs.@ 480°F.	160	213	162	43
2128	30.6	1 hr. @ 300°F.	188	450	225	45
	"	16 hrs.@ 480°F.	151	333	200	42
2129	52.0	1 hr. @ 300°F.	187	422	250	46
	"	16 hrs.@ 480°F.	226	260	125	58
2130	59.7	1 hr. @ 300°F.	178	422	250	45
	"	16 hrs.@ 480°F.	226	282	100	62

The stocks were compounded with SE-76 silicone gum.
The press cure was 15 minutes at 230°F.
2 per cent benzoyl peroxide was used as a curing agent, based on total silicone present.
Volume loading 20 percent based on pigment alone.

TABLE I-C-4

Celite 800 Coated with Vinyltrichlorosilane

Compound No.	Volume Loading	Silane Coating	Stress @ 200 percent	Tensile Strength p.s.i.	Elongation percent	Hardness Shore A
2101	10	None	77	229	438	19
2102	"	Vinyltrichloro(Linde)	70	204	450	16
2101-1	20	None	--	42	63	16
2102-1	"	Vinyltrichloro(Linde)	--	26	25	17
2101-2	30	None	--	120	50	56
2102-2	"	Vinyltrichloro(Linde)	--	135	50	59

The stocks were compounded with SE-76 silicone gum
The press cure was 15 minutes at 230°F
The oven cure was 1 hour at 300 F.
2 percent benzoyl peroxide was used as a curing agent

previously. The effect of this treatment was very slight and no significant changes were observed in the physical properties.

5. <u>Pigments Coated with Hydrocarbons and Alcohols</u>

We have previously given (Progress Report #10) results from compounding several pigments which had been coated with hydrolyzed monosilanes. It was found that surface coatings of vinyltrichloro-, methyldichloro-, and dimethyldichlorosilanes did not improve Santocel C, Celite 800 or Titanox RANC pigments. However, there was a decided improvement in Spheron 6 carbon black after it was given a coating of hydrolyzed vinyltrichlorosilane.

Recently, with the advent of GS199S Silica, our attention has been focussed on the effects of various hydrocarbon and alcohol coatings on silica pigments. In Section III of this report, our analysis of GS199S Silica is reported. We found it to be a fine amorphous silica containing an organic constituent which may be removed chemically or by distillation as a hydrocarbon or alcohol. We have coated two silica pigments with a hydrocarbon and several alcohols to see whether a simple coating would result in better reinforcing, or self curing pigment.

The procedure used was as follows: The pigment to be coated was heated to 200-400°F. under high vacuum to remove absorbed surface impurities. After this treatment it was then exposed directly to the vapors of the particular hydrocarbon or alcohol without contact with air, to insure absorption of the material on the surface. Absorption was continued until apparent equilibrium, and the weight gain of the pigment was recorded to determine the amount of coating. In this way 2 to 32 per cent by weight of alcohols were absorbed on the surface of Santocel C and Hi-Sil silica pigments.

Table I-C-5 gives the results of these experiments, and the compounding data. With Santocel C, a porous silica aerogel pigment, a 15 volume-2 per cent benzoyl peroxide control batch (#2084-1) gave: Tensile 450 p.s.i., Elongation 150 per cent and Hardness 57. With 3 per cent tert-amyl alcohol coating, a definite improvement is noted, with results being : Tensile 770 p.s.i., Elongation 300 per cent, and Hardness 59. Without any peroxide, the control gave: Tensile 130 p.s.i., Elongation 100 per cent and Hardness 42. This illustrates the considerable degree of reinforcement provided by this porous silica pigment alone. In addition to the 3 per cent tert-amyl alcohol, three coatings of 2, 4.2 and 8.5 per cent of isoamyl alcohol were applied. Compound No.2146, with 2 per cent isoamyl

TABLE I-C-5

Pigments Coated with Hydrocarbons and Alcohols

Compound No.	Coating	Recipe		Stress @ 200 percent	Stress @ 400 percent	Tensile Strength p. s. i.	Elongation percent	Hardness Shore A	Date
SANTOCEL-C									
2084-1	None	15 Vol-2%	B.P.	--	--	450	150	57	2/8/52
-2	3% tert-amyl alcohol	"	"	420	--	770	300	59	
-3	None	"	No B.P.	--	--	130	100	42	
-4	3% tert-amyl alcohol	"	"	--	--	170	75	59	
2153-3	4.2% iso-amyl alcohol	"	"			218	250	58	3/21/52
-4		"	2% B.P.			515	238	66	
2078-1	22% n-octane	"	"	486	--	670	263	60	1/30/52
-2			No B.P.	--	--	132	175	50	
2146-1	2% iso-amyl alcohol	"	"	137	176	206	500	66	3/6/52
-2			2% B.P.	427		574--	275	71	
2149-1	8.5% iso-amyl alcohol	"	No B.P.	All slabs cracked and could not be tested.				55	3/6/52
-2			2% B.P.					66	
HI-SIL									
2066-1	None	"	"	215		360	300	35	
-2	32% n-octane	"	"	226		309	288	38	
-3	None	"	No B.P.	--		0	0	22	
-4	32% n-octane	"	"	--		62	125	34	

TABLE I-C-5 (page 2)

Pigments Coated with Hydrocarbons and Alcohols

Compound No.	Coating	Recipe	Stress @ 200 percent	Stress @ 400 percent	Tensile Strength p. s. i.	Elongation percent	Hardness Shore A	Date
HI-SIL								
2077-1	None	15 vol 2% B.P.	290	--	278	188	38	
-2	11% tert-amyl alcohol	" "	179	--	286	300	30	
-3	None	" No B.P.	--	--	0	0	20	
-4	11% tert-amyl alcohol	" "	--	--	25	0	22	
2080-1	12% 2-methyl	" 2% B.P.	--	--	182	175	35	1/30/52
-2	heptanol	" No B.P.	--	--	83	163	30	

These stocks were compounded with G.E. SE-76
Press cure of 15 minutes at 230°F.
Oven cure of 1 hour at 300°F. for all samples.

alcohol, showed definite improvement in tensile strength and elongation both with and without peroxide.
Compound No.2153, with 4.2 per cent also showed increased cure over the control, to a lesser degree, while No.2149 with 8.5 per cent alcohol did not cure. Isoamyl alcohol thus induces some reinforcement without peroxide, and improves reinforcement when peroxide is used, but only at low concentrations of the order of 2 per cent.
N-octane coating, at 22 per cent by weight, gave definite improvements when peroxide was present, but did not aid curing in the absence of peroxide.
Hi-Sil silica pigment at 15 volumes and 2 per cent benzoyl peroxide gave 360 p.s.i. tensile, 300 per cent elongation, and 35 hardness, while without any peroxide, it gave no cure whatsoever. Thus Hi-Sil is distinctly inferior in vulcanizing power to Santocel C. Coatings of 32 per cent n-octane, 11 per cent tert-amyl alcohol, and 12 per cent 2-methyl heptanol did not improve its reinforcing properties with a benzoyl peroxide cure. However, these coatings did impart some strength, elongation and hardness to compounds where none existed with the Hi-Sil alone and no peroxide.
It thus appears that alcohols physically absorbed on the surface of a highly absorptive silica pigment aid in its reinforcing power for silicone rubber, and impart a very slight curing activity. It has not been determined whether this is due to an increase in pigment wettability, or to a chemical action between the coating and the silicone polymer.

II. COMPOUNDING WITH GS199S SILICA.

A. GS199S Silica in General Electric SE-76 Silicone Gum.

During the seven-month period from December 4,1951 to July 10, 1952, a large number of batches were mixed containing GS199S Silica in SE-76 silicone gum. Some of these mixes had as their objective high tensile strength, others improved heat resistance, others a comparison of various volume loadings, and still others a study of the effect of varying benzoyl peroxide concentrations. Since the mechanism by which GS199S Silica causes vulcanization to occur is not yet known, and since it has been found that varying results are obtained with different shipments of SE-76 rubber, results have not always been as consistent or as predictable as would be desired. For these reasons and because of the large amount of data to be reported it has been deemed advisable to present all of the data in composite tables:

Table II - A - 1.	Table II - A - 5.
" II - A - 2.	" II - A - 6.
" II - A - 3.	" II - A - 7.
" II - A - 4.	" II - A - 8.

These tables also include earlier data reported in Report #10 so that they contain all of the data obtained by our laboratory on GS199S Silica in SE-76 silicone gum up to July 10, 1952.

Table II-A-1 shows the earliest data obtained by using 5 and 10 volumes of GS199S Silica in SE-76 gum with and without preheating and using 2 per cent benzoyl peroxide. The low hardness figures and high elongation figures were considered unusual for a silica pigment.

The large amount of testing that has been carried out with 15 volume per cent loading is shown in Table II-A-2. It will be noticed that results in the first two lines of the Table are exceptionally low. It is now suspected that the laboratory technician who mixed these two batches neglected to incorporate benzoyl peroxide which would account for the low results. The rest of the first part of the Table shows that 15 volumes of GS199S Silica will result in tensile strengths running from 650 to 1540 p.s.i.with from approximately 200 to 750 per cent elongation depending on the concentration of benzoyl peroxide and the length and temperature of cure. It seems apparent that the highest properties are obtained with 300°F. cures and low percentages of benzoyl peroxide. Long cures at 400°F. appear to cause hardening and reduced elongations. The reader is referred to the notes at the bottom of Table II-A-1 which describe the two kinds of rubber which were used and the several shipments of

TABLE II-A-1

Oven Cure Study of 5 and 10 Volumes GS199S Silica in SE-76 with
2 Per cent Benzoyl Peroxide

Compound No.	GS199S	Gum	GS199S Vols.	Oven Cure	St. @ 200%	St. @ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
1967	A	1	5	1 hr. @ 300°F.	56	111	92	400	19	10/5/51	NPH
1967	"	"	5	"	53	----	64	300	19	"	PH
1967-1	A	1	10	1 hr. @ 300°F.	85	197	226	475	25	10/5/51	NPH
1967-1	"	"	10	"	104	---	195	338	25	"	PH

The following code applies to Tables II-A-1 through II-A-8 and Tables II-B-1 and II-B-2.

Gum No.	Gum Batch	Dates	Compound No.
1	SE-76 B5946	to 5/8/52	to 2224
2	SE-76 11317-3	5/8/52 to 7/10/52	2225 on

GS199S No.	Shipment	Dates
A	GS199S Expt. 1st shipment.	10/5/51
B	GS199S Expt. 2nd shipment.	12/5/51
C	GS199S Expt. 3rd shipment.	1/30/52
D	Pilot Plant Lot.	

TABLE II-A-2

Oven Cure Study of 15 Volumes GS199S Silica in SE-76 with
Varying Amounts of Benzoyl Peroxide

Compound No.	GS199S	Gum	Per cent Benzoyl Peroxide	Oven Cure	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
1967-2	A	1	2.0	1 hr. @ 300°F.	172	---	280	375	37	10/5/51	NPH
"	"	"	"	"	171	---	247	300	40	"	PH
2050	"	"	0.5	24 hrs. @ 300°F.	288	520	1540	750	60	12/14/51	
2050-1	"	"	1.0	"	374	740	840	475	63	"	
2050-2	"	"	1.5	"	487	960	960	400	65	"	
1967-2	"	"	2.0	"	573	---	782	313	69	11/7/51	
1967-2	"	"	"	"	597	---	975	350	68	12/14/51	
2050	"	"	0.5	24 hrs. @ 400°F.	622	---	822	350	73	"	
2050-1	"	"	1.0	"	630	---	710	275	70	"	
2050-2	"	"	1.5	"	---	---	870	275	73	"	
1967-2	"	"	2.0	"	675	---	650	188	73	11/7/51	
1967-2	"	"	"	"	795	---	795	200	76	12/14/51	
1967-2	B	1	2.0	1 hr. @ 300°F.	346	727	1008	525	61	12/18/51	
1967-2	C	1	2.0	1 hr. @ 300°F.	242	542	1170	613	61	1/30/52	
1967 P	D	"	"	"	428	814	833	413	59	5/27/52	
1967-2	C	"	"	1 hr. @ 400°F.	441	910	935	425	50	1/30/52	
2265-1	C	2	0.0	12 hrs. @ 400°F.	155	226	278	512	44	6/27/52	
2265-2	"	"	0.5	"	287	455	567	525	55	"	
2265-3	"	"	1.0	"	353	592	678	475	63	"	
2225-A	"	"	0.5	24 hrs. @ 400°F.	370	575	580	425	61	5/15/52	
2265-1	"	"	0.0	44 hrs. @ 400°F.	353	---	362	225	64	7/3/52	
2265-2	"	"	0.5	"	444	---	454	208	67	"	

TABLE II-A-2 (Cont. pg. 12)

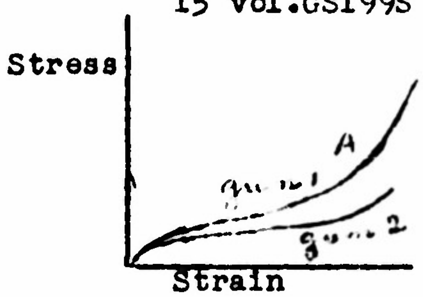
Oven Cure Study of 15 Volumes GS199S Silica in SE-76 with
Varying Amounts of Benzoyl Peroxide

Compound No.	GS199S	Gum	Per cent Benzoyl Peroxide	Oven Cure	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
2265-3	C	2	1.0	44 hrs. @ 400°F.	404	---	425	163	71	7/3/52	
2265-B	"	"	0.5	24 hrs. @ 480°F.	---	---	342	50	70	5/15/52	
2265-1	"	"	0.0	12 hrs. @ 400°F. 16 hrs. @ 480°F.	---	---	348	50	70	6/3/52	
2265-2	"	"	0.5	"	---	---	325	75	67	"	
2265-3	"	"	1.0	"	---	---	314	63	68	"	

GS199S Silica which were tested.

The lower part of Table II-A-2 shows the results on various benzoyl peroxide mixings with gum No.2 in which an attempt was made to duplicate the original high tensiles obtained with 15 volumes GS199S Silica in SE-76 silicone gum. At the same time it was realized that 400 or 480°F. curing would be desirable for these stocks as it is for most ordinary silicone compounds. The data show first of all that a shipment of rubber labelled "2" lacks ability to develop high tensile strength although the elongation and hardness results are similar to those obtained with the earlier gum labelled "1". When stress-strain curves are drawn on compounds from the two shipments of gum, they clearly reveal that the deficiency of Gum #2 is evident only in the upper portion of the curve labelled A in the sketch below:

Typical Stress-Strain Curves
15 vol.GS199S in SE-76 (1 hr. @ 300°F.)



In Table II-A-2 as in others to follow, those cures carried out at 480°F. almost invariably resulted in a brittle condition of the test piece which is characterized by elongations of from zero to 75 per cent. Test strips cured at 480°F. cannot withstand bending double without breaking. The inability to control this heat hardening at curing temperatures or aging temperatures of 400-500°F. is at the present time one of the serious defects of GS199S Silica.

Table II-A-3 contains all of the mixings with 25 volumes of GS199S Silica in SE-76 gum and containing varying amounts of benzoyl peroxide. It is apparent that this volume loading results in the highest tensiles. Again, cures obtained at 300°F. have higher tensiles and elongations than those obtained at 400°F. With long cures at 400°F. the heat embrittlement mentioned above is beginning to make itself felt.

The lower part of the Table shows that 25 volume of GS199S Silica is not a sufficient factor in the production of high physical properties with gum #2 especially if long cures at 400°F. are used.

Experiments in which 20, 27.5, 30, 35 and 40 volumes GS199S Silica were used are covered in Table II-A-4. All this work was done with the older gum (#1). At 40 volumes mixing becomes difficult. With great care to add the pigment slowly, as much as 52.5 per cent of GS199S Silica can be introduced into SE-76. At this loading, however, the mix becomes

TABLE II-A-3

Oven Cure Study of 25 Volumes GS199S Silica in SE-76 with

Varying Amounts of Benzoyl Peroxide

Compound No.	GS199S	Gum	Per cent Benzoyl Peroxide	Oven Cure	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
1985	A	1	0.0	1 hr. @ 300°F.	419	793	1615	613	77	11/26/51	
1996	"	"	1.0	"	276	481	1930	850	73	"	
1996-1	"	"	1.5	"	308	583	1680	700	75	"	
1967-4	"	"	2.0	"	335	648	1285	625	70	10/15/51	NPH
"	"	"	"	"	379	810	1400	563	70	"	PH
1985	"	"	0.0	24 hrs. @ 300°F.	684	1205	1170	388	85	11/26/51	
1996-2	"	"	0.5	"	480	875	1540	588	81	12/14/51	
1996	"	"	1.0	"	554	1000	1660	550	83	11/26/51	
1996-1	"	"	1.5	"	610	1110	1325	463	85	"	
1985-1	"	"	1.65	"	285	485	1685	788	72	11/6/51	
1985	"	"	2.0	"	219	367	1415	800	65	11/7/51	
1985	"	"	0.0	24 hrs. @ 400°F.	---	---	795	75	93	11/26/51	
1996-2	"	"	0.5	"	---	---	679	75	91	12/10/51	
1996	"	"	1.0	"	---	---	795	63	93	11/26/51	
1996-1	"	"	1.5	"	---	---	795	75	94	"	
1985-1	"	"	1.65	"	---	---	731	88	93	11/6/51	
1985	"	"	2.0	"	700	---	1035	350	82	11/7/51	
1985-1	"	"	1.65	24 hrs. @ 300°F. + 15 hrs. @ 350°F.	539	945	1395	550	80	11/9/51	
1985	"	"	2.0	"	392	686	1160	600	73	11/7/51	
1985	"	"	2.0	24-36 hrs. @480°F.			Too brittle to test.		95	10/30/51	
1985	B	1	2.0	1 hr. @ 300°F.	410	795	1670	625	80	12/19/51	
1962-4	"	"	"	"	533	---	576	225	71	1/7/52	
1985 P	D	1	2.0	1 hr. @ 300°F.	523	1160	1289	463	77	2/27/52	
1985	C	"	"	"	320	663	1687	663	70	1/30/52	

TABLE II-A-3

Oven Cure Study of 25 Volumes GS199S Silica in SE-76 with Varying Amounts of Benzoyl Peroxide (Cont. pg. 2)

Compound No.	GS199S	Gum	Per cent Benzoyl Peroxide	Oven Cure	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
1985	C	1	2.0	1 hr. @ 400°F.	455	870	1505	550	80	1/30/52	
1985	"	"	"	"	384	795	1685	650	67	2/4/52	Black (+2% P-33)
"	"	"	"	"	403	833	1710	625	68	"	White (+5% TiO_2)
1985	"	"	"	1.5 hrs. @ 480°F.	867	---	867	200	--	2/13/52	
2266-1	C	2	0.0	12 hrs. @ 400°F.	314	478	819	650	72	6/27/52	
2266-2	"	"	0.5	"	477	772	897	525	81	"	
2266-3	"	"	1.0	"	552	868	915	412	82	"	
2266-1	"	"	0.0	44 hrs. @ 400°F.	---	---	494	50	65	7/3/52	
2266-2	"	"	0.5	"	---	---	518	50	83	"	
2266-3	"	"	1.0	"	---	---	530	25	88	"	
2266-1	"	"	0.0	12 hrs. @ 400°F. + 16 hrs. @ 480°F.	---	---	39	6	93	6/3/52	
2266-2	"	"	0.5	"	---	---	449	12	92	"	
2266-3	"	"	1.0	"	---	---	234	25	94	"	

TABLE II-A-4

Oven Cure Study of Varying Volumes of GS199S Silica in SE-76
with Benzoyl Peroxide Present

Compound No.	GS199S	Gum	GS199S Vols.	Per cent Benzoyl Peroxide	Oven Cure	St. @ 200%	St. @ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
1967-3	A	1	20	2.0	1 hr. @ 300°F.	203	399	591	563	43	10/5/51	NPH
"	"	"	"	"	"	248	---	321	275	43	"	PH
1967-3	"	"	"	"	24 hrs. @ 300°F.	520	960	987	425	75	11/1/51	
"	"	"	"	"	24 hrs. @ 400°F.	---	---	589	75	84	"	
2131	C	1	"	"	1 hr. @ 300°F.	372	820	1900	625	68	3/3/52	
1962-5	B	1	27.5	2.0	1 hr. @ 300°F.	582	---	694	263	73	1/7/52	
1967-5	A	1	30	2.0	1 hr. @ 300°F.	485	925	1365	525	80	10/15/51	NPH
"	"	"	"	"	"	361	731	1096	500	70	"	PH
2055	B	1	35	1.0	1 hr. @ 300°F.	370	660	1490	663	86	1/2/52	
1967-6	A	1	40	2.0	1 hr. @ 300°F.	Too much pigment.					10/15/51	

very hot on the mill and it is not practical to add benzoyl peroxide. Since silica cures the rubber without benzoyl peroxide, the latter is not needed. These high loadings result in a mica-like substance when heated at curing temperatures. They do retain some flexibility and may eventually find some use.

Table II-A-5 contains data on 5 and 10 volumes GS199S Silica in SE-76 gum with no benzoyl peroxide added. With Gum #1 it was apparent that 5 volumes of the pigment was insufficient to cause very much curing to occur although some cure was evident. At 10 volumes, however, a definite cure occurred in the absence of benzoyl peroxide. This was also true with Gum #2 which in this case was cured at 480°F. Here, because of the low concentration of GS199S Silica cured compounds were less brittle than when higher volumes of pigment were used.

Data for all those mixings containing 15 volumes GS199S Silica in SE-76 gum in the absence of benzoyl peroxide are compiled in Table II-A-6. With low temperature cures, for example, one hour at 300°F., it may be noted that high elongation and low hardness compounds result. Even when the cures are as severe as 24 hours at 400°F. high tensiles and high elongations and hardness of approximately 60 are found, at least with Gum #1. In one or two cases cures at 480°F. were

TABLE II-A-5

Oven Cure Study of 5 and 10 Volumes GS199S Silica in SE-76 (No Benzoyl Peroxide)

Compound No.	GS199S	Gum	GS199S Vols.	Oven Cure	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
1967-A	B	1	5	5 hrs. @ 400°F.	26	43	68	613	31	1/18/52	
1967-A	C	1	5	24 hrs. @ 300°F.	28	--	32	463	11	3/13/52	
"	"	"	"	24 hrs. @ 400°F.	29	--	35	263	12	3/13/52	
1967-1A	B	1	10	5 hrs. @ 400°F.	62	169	515	888	71	1/18/52	
1967-1A	C	1	"	24 hrs. @ 300°F.	81	148	574	925	26	3/13/52	
"	"	"	"	24 hrs. @ 400°F.	128	280	594	675	36	"	
2261-A	C	2	"	1 hr. @ 480°F.	143	--	199	350	35	6/17/52	Cure started 300°F.
2261-B	"	"	"	4 hrs. @ 480°F.	--	--	158	163	45	"	
2261-C	"	"	"	8 hrs. @ 480°F.	--	--	176	138	43	"	
2261-D	"	"	"	"	--	--	170	163	43	"	
2261-E	"	"	"	16 hrs. @ 480°F.	--	--	131	113	43	"	

TABLE II-A-6

Oven Cure Study of 15 Volumes GS199S Silica in SE-76
(No Benzoyl Peroxide)

Compound No.	GS199S	Gum	Oven Cure	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
2154-3	A	1	16 hrs. @ 400°F.	512	785	885	475	68	5/15/52	
2050-1	"	"	24 hrs. @ 400°F.	622	---	822	350	73	"	
1967-2A	B	1	No cure	71	94	424	1050	30	1/2/52	
1967-2A	"	"	1 hr. @ 300°F.	83	143	1025	1150	37	1/2/52	
"	"	"	"	93	165	876	1050	36	1/2/52	
"	"	"	"	96	160	860	1000	37	"	
"	"	"	"	94	141	824	1025	36	"	
1967-2A	"	"	24 hrs. @ 300°F.	210	383	1660	913	53	12/14/51	
1967-2A	"	"	24 hrs. @ 400°F.	387	645	1160	638	63	12/10/51	
1967-2A	C	1	1 hr. @ 300°F.	150	225	467	1025	32	1/30/52	
1967-2A	"	"	24 hrs. @ 300°F.	147	240	1430	950	41	3/13/52	
2204	"	"	16 hrs. @ 400°F.	277	508	1415	750	59	5/2/52	
"	"	"	"	284	508	1368	762	59	"	
2204-1	"	"	"	265	489	1378	750	57	"	
"	"	"	"	274	498	1492	775	58	"	
2204-2	"	"	"	290	520	1435	725	59	"	
"	"	"	"	294	557	1360	732	60	"	
2204-3	"	"	"	299	523	1300	732	60	5/7/52	
"	"	"	"	295	516	1125	675	60	"	
1967-2A	"	"	24 hrs. @ 400°F.	250	500	1400	725	--	2/12/52	Black
1967-2A	"	"	"	234	440	1205	750	50	"	"
1967-2A	"	"	"	343	854	1265	638	53	"	

TABLE II-A-6

Oven Cure Study of 15 Volumes GS199S Silica in SE-76
(No Benzoyl Peroxide) (Cont. pg. 2)

Compound No.	GS199S	Gum	Oven Cure	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
1967-2A	C	1	16 hrs. @ 430°F.	750	---	903	275	75	5/21/52	
1967-2A	"	"	24 hrs. @ 400°F. 3 hrs. @ 480°F.	425	800	1097	675	50	2/12/52	
1967-2A	"	"	24 hrs. @ 400°F. 19 hrs. @ 480°F.	430	---	710	375	60	"	
2240-A	C	2	None	39	51	103	888	25	5/27/52	
2240-B	"	"	0.5 hr. @ 400°F.	62	87	171	837	34	"	
2240-C	"	"	1 hr. @ 400°F.	74	99	227	838	36	"	
2240-D	"	"	4 hrs. @ 400°F.	99	148	321	775	39	"	
2240-E	"	"	16 hrs. @ 400°F.	208	338	501	675	50	"	
2226-A	"	"	24 hrs. @ 400°F.	---	---	356	175	68	5/15/52	
2284	"	"	"	254	440	440	400	55	7/3/52	
2225-A	"	"	Cycle to 400°F.	94	144	308	875	41	5/23/52	
2225-B	"	"	Cycle to 450°F.	171	274	390	600	48	"	
2262-A	"	"	1 hr. @ 480°F.	---	---	400	300	57	6/17/52	
2262-B	"	"	4 hrs. @ 480°F.	---	---	351	100	60	"	
2262-C	"	"	8 hrs. @ 480°F.	---	---	339	83	71	"	
2262-D	"	"	"	---	---	344	75	50	"	
2262-E	"	"	16 hrs. @ 480°F.	---	---	291	50	72	"	
2225-C	"	"	Cycle to 480°F.	308	---	425	325	58	5/23/52	
2284	"	"	24 hrs. @ 400°F. 9 hrs. @ 480°F.	356	---	380	117	58	7/8/52	
2225-D	"	"	Cycle to 480°F. 16 hrs. @ 480°F.	---	---	296	50	71	5/23/52	

carried out without embrittlement resulting. Allowing for possible inaccuracy of a few degrees in oven temperature it is still evident that high temperature curing can be carried out in the absence of benzoyl peroxide and with a 15 volume loading of GS199S Silica without encountering the embrittlement. The method of reproducing this resistance to heat at will is not known.

Starting in May of 1952, Gum #2 resulted in lower tensiles and some reduction in elongation. A cure range studied at 400°F. indicated an optimum time of curing at this temperature to be approximately 16 hours. At this temperature compounds would not become brittle upon curing up to 24 hours. However, when cured at 480°F. they became brittle in 4 to 8 hours.

Similar data were obtained, as shown in Table II-A-7, with 25 volumes GS199S Silica in the absence of benzoyl peroxide. Here the tensile strengths are higher than those obtained at 15 volumes pigment and elongation somewhat lower. The hardness runs from 50 to 90 depending on the degree of cure.

With Gum #2 optimum properties are again obtained with 16 hours cure at 400°F.

TABLE II-A-7

Oven Cure Study of 25 Volumes GS199S Silica in SE-76

(No Benzoyl Peroxide)

Compound No.	GS199S	Gum	Oven Cure	St. @ 200%	St. @ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
1985-A	A	1	1 hr. @ 300°F.	165	247	1245	1000	62	12/3/51	
"	"	"	24 hrs. @ 300°F.	298	535	1720	775	70	"	
1985-A	"	"	24 hrs. @ 400°F.	782	---	897	275	89	12/10/51	Tan, transparent
"	"	"	"	708	---	1205	375	89	"	White, opaque
1985-A	B	1	22 hrs. @ 300°F.	225	402	1540	850	67	1/21/52	White(+5% TiO_2)
"	"	"	"	226	388	1515	900	66	"	Black (+2% P-33)
"	"	"	16 hrs. @ 400°F.	667	---	850	300	82	1/19/52	White(+5% TiO_2)
"	"	"	"	541	925	1030	450	80	"	Black (+2% P-33)
"	"	"	24 hrs. @ 400°F.	780	---	1050	325	89	"	White(+5% TiO_2)
"	"	"	"	96	169	925	975	58	1/15/52	
1985-A	C	1	1 hr. @ 300°F.	122	171	1025	1050	52	1/30/52	
2229-1B	"	"	24 hrs. @ 300°F.	260	480	1785	850	66	6/1/52	
1985-A	"	"	1 hr. @ 400°F.	179	274	1695	900	56	4/30/52	
"	"	"	"	117	288	1310	875	52	"	Aged 21 days @125°F. remilled before cure.
2229-1A	"	"	1 hr. @ 400°F.	170	325	1445	925	62	6/1/52	
1985-A(A1)	"	"	1 hr. @ 400°F.	217	368	1768	800	64	6/9/52	
2205	"	"	16 hrs. @ 400°F.	548	966	1430	525	80	5/2/52	
"	"	"	"	418	874	1343	525	74	"	
2205-1	"	"	"	508	978	1507	550	80	"	
"	"	"	"	545	1042	1612	550	80	"	
2205-2	"	"	"	578	1048	1463	525	84	"	
"	"	"	"	573	1050	1471	525	83	"	
2205-3	"	"	"	560	1030	1460	512	83	"	

TABLE II-A-7

Oven Cure Study of 25 Volumes GS199S Silica in SE-76

(No Benzoyl Peroxide) (Contd.pg.2)

Compound No.	GS199S	Gum	Oven Cure	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
2205-3	C	1	16 hrs.@ 400°F.	640	---	1035	450	84	5/2/52	
1985-A	"	"	24 hrs.@ 400°F.	448	885	1590	563	--	2/12/52	Black
"	"	"	"	455	885	1250	525	72	"	"
2229-1C	"	"	"	585	1070	1200	475	80	6/1/52	
1985-A	"	"	"	640	---	1128	375	66	2/12/52	
"	"	"	+ 3 hrs.@ 480°F. 24 hrs.@ 400°F. + 19 hrs.@ 480°F.	---	---	803	75	85	"	
2269-2	C	2	None	---	---	185	462	47	6/27/52	
2264-A	"	"	1 hr.@ 300°F.	76	99	235	862	52	6/14/52	
2264-B	"	"	24 hrs.@ 300°F.	143	220	585	837	57	"	
2229-C	"	"	"	184	271	690	825	66	5/22/52	
2241-A	"	"	None	83	100	193	913	51	5/27/52	
2241-B	"	"	0.5 hrs.@ 400°F.	121	158	296	788	60	"	
2241-C	"	"	1 hr.@ 400°F.	163	202	382	763	62	"	
2229-A	"	"	"	167	226	495	837	65	5/22/52	
2241-D	"	"	4 hrs.@ 400°F.	211	308	621	725	70	5/27/52	
2241-E	"	"	16 hrs.@ 400°F.	503	810	1059	525	80	5/22/52	
2229-B	"	"	24 hrs.@ 400°F.	570	915	965	425	80	"	
2285	"	"	"	508	837	798	375	75	7/3/52	
2248-A	"	"	1 hr.@ 480°F.	---	---	716	450	74	6/4/52	
2270-1	"	"	3 hrs.@ 480°F.	---	---	565	100	80	6/25/52	
2270-2	"	"	"	610	---	695	275	75		
2270-3	"	"		610	---	610	200	73	"	
2248-B	"	"	4 hrs.@ 480°F.	---	---	580	50	87	6/4/52	
2248-C	"	"	7 hrs.@ 480°F.	---	---	577	25	90		
2270-1	"	"	12 hrs.@ 480°F	---	---	451	25	89	6/25/52	
2270-2	"	"	"	---	---	613	75	84	"	
2270-3	"	"	"	---	---	538	50	83	"	

TABLE II-A-7

Oven Cure Study of 25 Volumes GS199S Silica in SE-76
(No Benzoyl Peroxide) (Cont. pg. 3)

Compound No.	GS199S	Gum	Oven Cure	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
2248-D	C	2	16 hrs. @ 480°F.	---	---	402	< 25	92	6/4/52	
2248-E	"	"	24 hrs. @ 480°F.	---	---	454	< 25	94	"	
2269-2	"	"	1 hr. @ 300°F. + 16 hrs. @ 400°F.	---	---	538	300	77	7/10/52	
2285	"	"	24 hrs. @ 400°F. + 9 hrs. @ 480°F.	---	---	583	88	83	7/8/52	
2269-2	"	"	16 hrs. @ 420°F. + 1 hr. @ 480°F.	---	---	721	50	85	7/10/52	

TABLE II-A-8

Oven Cure Study of Varying Volumes of GS199S Silica in SE-76 in the Absence of Benzoyl Peroxide

Compound No.	GS199S	Gum	GS199S Vols.	Oven Cure	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
2070	B	1	19.2	24 hrs. @ 400°F.	86	137	860	>1200	43	1/15/52	
2131-A	C	1	20	1 hr. @ 300°F.	152	228	1240	900	52	2/2/52	
2286	C	1	30	24 hrs. @ 400°F.	---	---	734	150	89	7/3/52	
2286	"	"	"	24 hrs. @ 400°F. + 9 hrs. @ 480°F.	---	---	150	0	93	7/8/52	
I	C	1	35	1 hr. @ 400°F.	345	530	1220	700	75	4/8/52	
II	"	"	"	"	202	300	1125	900	72	"	
2287	C	2	35	24 hrs. @ 400°F.	---	---	731	63	93	7/3/52	
2272-1A	"	"	"	3 hrs. @ 480°F.	---	---	264	<25	93	6/25/52	
2272-2A	"	"	"	"	---	---	675	50	90	"	
2287	"	"	"	24 hrs. @ 400°F. + 9 hrs. @ 480°F.	---	---	135	0	95	7/8/52	

Table II-A-8 contains other miscellaneous data obtained on loadings of 19.2, 20, 30 and 35 volumes GS199S Silica in the absence of benzoyl peroxide. With the higher volume loadings the tendency to shortness especially when cured at 400°F. or 480°F. is more pronounced.

B. Special Samples of GS199S Silica.

Table II-B-1 contains data on compound #2139 which was made from a Banbury mix of GS199S and SE-76 rubber by one of the du Pont Laboratories. So much reinforcement, probably due to heat, occurred during preparation of the Banbury mix that it could no longer be cured even when mixed with fresh gum. In another trial a Banbury master batch made at lower temperature was diluted with new rubber to a 25 volume concentration and cures were obtained on this #2162-1 compound. It was evident that the rubber used in preparation in this master batch was similar to that called #2 in previous Tables. In compound #2162-3, rubber received from the du Pont Laboratories was mixed with GS199S Silica and low physical properties resulted again probably due to inferior grade of rubber. In #2163-2 the du Pont M.B. was diluted with another (10 vol.) M.B. to yield a 25 vol. batch in the hope that two master batches would mix together better. Again poor results were obtained.

TABLE II-B-1

Special GS199S Silica Samples from DuPont

Compound No.	Description of Batch and GS199S	Oven Cure	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date	Remarks
2139	DuPont Banbury mix of GS199S & SE-76 1:1 dil. to 15 vols. with SE-76 on mill and cured.	1 hr. @ 300°F. +16 " @ 480°F.			No Cure			3/5/52	
2140	Same treatment, 3% benzoyl peroxide added.	"	--	--	54	25	40	"	
2162-1	DuPont Banbury MB 1:1 dil. with SE-76 to 25 vol.	1 hr. @ 300°F. +16 " @ 400-480°F.	160 --	208 --	618 564	900 50	59 89	3/27/52	
2162-3	DuPont SE-76 + GS199S 25 vol.	1 hr. @ 300°F.	122	134	208	700	62		
2162-3	" " " " "	"	120	141	330	875	55		
2162-3	" " " " "	24 " @ 400°F.	590	---	888	363	82		
2163-1	Regular mix 25 vol. control	1 hr. @ 300°F.	300	196	878	975	62		
2163-2	Du Pont Banbury MB 1:1 diluted with Regular mix 10 vol to yield a 25 vol. batch	1 hr. @ 300°F. +24 " @ 400°F.	227 ---	-- --	234 440	263 125	56 74		

In another series of mixings dimethyldichlorosilane, trimethyl chlorosilane, LT35 silicone oil, P33 carbon black and steam were each applied to GS199S Silica to reduce dusting which occurs when the pigment is added to the rubber on the mill. Physical test data are given in Table II-B-2. The chemicals and carbon black were stirred into the pigment in a beaker. The steam was squirted out over the bank of pigment on the mill. None of the added ingredients altered the tensile or other chemical properties appreciably except the two silanes which caused the slab to crack while in the mold. The use of a fairly heavy cloud of steam blowing across the pigment on the mill had a visible effect in reducing the flying of the charged silica particles. Evidently the moisture served to remove static charges from the silica even though it did not wet the silica. The use of an ultraviolet light at a distance of about one foot had no visible effect. It is felt from this experiment that proper humidity control would be essential in a mill room in which GS199S Silica was being milled into silicone rubber.

A sample of GS Silica was received in March 1952, bearing the label Pilot Plant GS199S. This sample should no longer be considered representative of the

TABLE II-B-2

Compounding GS199S Silica with other Ingredients in the Absence of Benzoyl Peroxide

Compound No.	GS199S	Gum	Per cent Benzoyl Peroxide	Other and Vol.	St.@ 200%	St.@ 400%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A	Date
2060-1	C	1	None	Control	594	1050	1252	475	80	3/21/52
2060-2	"	"		2% $(CH_3)_2SiCl_2$		Slab	cracked		94	
2060-3	"	"		2% $(CH_3)_2SiCl_2$		"	"		82	
2060-4	"	"		16.3% LT-35	567	995	1168	450	79	
2060-5	"	"		10% P-33	449	829	1382	575	76	
2060-6	"	"		1% P-33	442	808	1355	588	77	
2060-7	"	"		Steam jet (light)	590	1035	1305	475	79	
2060-8	"	"		" " (heavy)	433	823	1635	600	71	
2060-9	"	"		Ultraviolet lamp	626	1136	1393	463	87	

TABLE II-B-3

EVALUATION OF PILOT PLANT GS199S AT VARIABLE LOADING

Compound No.	Volume Loading	Oven Cure	Stress @ 200%	Stress @ 400%	Tensile Strength p. s. i.	Elongation Percent	Hardness Shore A
2164-1	10	1 hr. @ 300°F.	40	48	67	700	13
2189-1	"	24 " @ 300°F.	116	151	442	900	36
2189-1	"	1 " @ 400°F.	81	114	252	850	30
2189-1	"	16 " @ 400°F.	204	308	314	412	42
2164-1	"	24 " @ 400°F.	153	254	308	488	33
2164-2	15	1 " @ 300°F.	52	78	182	975	26
2189-2	"	24 " @ 300°F.	162	263	827	832	50
2189-2	"	1 " @ 400°F.	137	204	590	925	46
2189-2	"	16 " @ 400°F.	403	655	675	500	66
2164-2	"	24 " @ 400°F.	300	493	1012	675	43
2164-3	25	1 " @ 300°F.	116	174	704	900	48
2189-3	"	24 " @ 300°F.	226	411	1275	732	62
2189-3	"	1 " @ 400°F.	194	318	1105	800	59
2189-3	"	16 " @ 400°F.	670	--	725	212	84
2164-3	"	24 " @ 400°F.	550	1005	1166	475	75
2164-4	35	1 " @ 300°F.	185	217	739	875	69
2189-4	"	24 " @ 300°F	293	487	1085	675	83
2189-4	"	1 " @ 400°F.	245	412	1050	750	75
2189-4	"	16 " @ 400°F.	--	--	260	0	94
2164-4	"	24 " @ 400°F.	774	--	818	250	85
2164-5	52.5	1 " @ 300°F.	400	405	602	675	87
2164-5	"	24 " @ 400°F.		Brittle slab			96

The stocks were compounded with SE-76 silicone gum(Batch #5946)
No benzoyl peroxide was used as a curing agent.
Press cure was 15 minutes at 230°F.

GS Silica which will be turned out from the Du Pont Pilot Plant since minor changes will be made in the properties of the pigment before Pilot Plant samples actually appear.

This sample had an apparent density about three times as great as that of the regular GS199S Silica received up to this time. Aggregates were also larger. Obviously, it was hoped that this material would be equally satisfactory but such was not the case. Data in Table II-B-3 show that this Pilot Plant sample was slower to develop high tensile strength even at 400°F. and it did not develop as high a tensile strength as the finer samples.

C. <u>The Use of GS199S Silica as a Curing Agent with other pigments</u>

Since GS199S Silica has the property of curing as well as reinforcing silicone rubber, it was obvious that it should be tried with other cheaper pigments as diluents. Santocel C, being the most like GS199S Silica, was tried first. Data are shown, Table II-C-1, using various combinations of GS199S Silica and Santocel C. Two recipes, 1962-2A and 1962-3A, in which Santocel C alone was used in the absence of benzoyl peroxide resulted in only slight cure. When 5 and 10 volumes of GS199S Silica were added to the Santocel C recipes,

TABLE II-C-1

GS199S Silica and Santocel C

Compound No.	Santocel C Vols per 100 Gum	GS199S Vols per 100 Gum	Benzoyl Peroxide Wt. %	Oven Cure	Stress @ 200%	Tensile Strength p.s.i.	Elongation %	Hardness Shore A
1962-2A	15	--	--	24 hrs. @ 400°F.	127	162	350	46
1967-1A	--	10	--	5 " @ 400°F.	82	515	888	71
2060-1	15	10	--	22 " @ 400°F.	537	760	300	82
1962-3A	20	--	--	24 " @ 400°F.	260	286	225	67
1967-A	--	5	--	5 " @ 400°F.	26	68	613	31
2060-2	20	5	--	22 " @ 400°F.	--	470	138	84
1985-2A		15	--	24 " @ 400°F.	387	1160	638	63
1985-A		25	--	24 @ 400°F.	782	897	275	89

The stocks were compounded with G.E. SE-76 silicone gum (Batch "5946)
Press cure was 15 minutes at 230°F.

they stiffened and hardened appreciably; but the results were not nearly as good as those usually obtained with a total of 25 volumes of GS199S Silica alone.

Titanox RANC when used with 2 per cent benzoyl peroxide and with a 40 volume loading of the pigment usually gives a tensile of approximately 500 p.s.i. with 400 per cent elongation. When GS199S Silica was introduced in a recipe containing 40 volumes Titanox RANC in the absence of benzoyl peroxide, inferior results were obtained. The Titanox RANC was reduced as the percentage of GS199S Silica was increased. When approximately equal volumes of Titanox RANC and GS199S Silica were used, the results were approximately the same as when Titanox RANC was used alone with 2 per cent benzoyl peroxide. (See page 23 of Report No.8). The only difference was that the mixture of 20 to 25 volumes Titanox RANC and 20 to 25 volumes of GS199S Silica in the absence of benzoyl peroxide resulted in elongations as high as 600 per cent.

Another way of looking at these same results is that 20 volumes of Titanox RANC added to a 25 volume GS199S Silica recipe drops the tensile from 1200-1700 p.s.i. to 500-600 p.s.i. with very little other change in the properties. The results are given in Table II-C-2.

TABLE II-C-2

GS199S and Titanox RANC

Compound No.	Titanox RANC Vols per 100 vols gum	GS199S Vols per 100 vols gum	Treatment of Titanium Dioxide	Oven cure	Physical Properties: Stress @ 200%	Physical Properties: Tensile Strength p.s.i.	Physical Properties: Elongation %	Hardness Shore A
1967-A	--	5	--	5 hrs. @ 400°F.	26	68	613	31
1967-1A	--	10	--	5 " @ 400°F.	82	515	888	71
1967-2A	--	15	--	24 " @ 300°F.	210	1660	913	53
1967-3A	--	25	--	24 " @ 300°F.	298	1720	775	70
2076	40	5	Htd.@ 500°F, preheated	16 " @ 400°F.	--	99	75	48
2076-1	40	10	"	"	--	211	75	70
2085	30	15	"	24 " @ 300°F.	218	333	463	58
2086	25	20	"	"	235	463	613	63
2087	20	25	"	"	253	570	625	68

The stocks were compounded with G.E. SE-76 silicone gum (Batch #5946)
The press cure was 15 minutes at 830°F.

Mixtures similar to those above were made with GS199S Silica and Spheron 6. As is usual with carbon blacks, very poor results were obtained and the presence of 5 or 10 volumes of GS199S Silica did not improve the results notably. They are, therefore, not given in detail.

Increasing volumes of Celite Superfloss were added to 15 volume recipes of GS199S Silica both with and without added benzoyl peroxide. All cures were made at 16 hours at 400°F. As would be expected, Celite Superfloss caused a lowering of tensile and elongation and a raising of the hardness and modulus. It is well known that Celite Superfloss is an ideal diluent for silicone compounds since it does not cause a rapid lowering of properties. Beyond the first 5 per cent of Celite Superfloss that was added the properties held up verywell. The results are best seen by examining Table II-C-3. The use of Celite Superfloss is definitely indicated as a cheapening agent for GS199S Silica.

A special series of Titanox samples obtained by Titanium Pigment Corporation was available. Because of their fineness and reactivity, poor results had been obtained when these samples were used with benzoyl peroxide. Accordingly, they were added, in 10 volume quantities, to 15 volume GS199S Silica. Results are

TABLE II-C-3

STOCKS OF 15 VOLUMES GS199S AND VARIABLE LOADINGS OF CELITE SUPER FLOSS

Compound No.	Volumes of Celite Super Floss	Percent Benzoyl Peroxide	Stress @ 200%	Tensile Strength p. s. i.	Elongation %	Hardness Shore A
2154-1	None	None	303	1376	713	58
2154-2	"	2.0	700	932	300	70
2154-3	5.0	None	349	845	563	57
2154-4	"	2.0	846	900	225	71
2154-5	10.0	None	467	813	463	61
2154-6	"	2.0	909	910	200	77
2154-7	15.0	None	519	885	475	68
2154-8	"	2.0	--	660	68	84
2154-9	20.0	None	594	730	325	71
2154-10	"	2.0	--	726	68	84
2154-11	40.0	None	--	718	125	88
2154-12	"	2.0	--	464	75	91

The stocks were compounded with G.E. SE-76 silicone gum (Batch #5946)
The press cure was 15 minutes at 230°F.
The oven cure was 16 hours at 400°F.

presented in Table II-C-4 simply to show that GS199S Silica offers a way of using pigments, such as these, which tend to interfere with the vulcanizing action of benzoyl peroxide.

Mercurous Oxide is a common ingredient for low compression set silicone compounds. It is believed that the action of mercurous oxide is primarily to clean up traces of benzoic acid in the system before they have a chance to exert a depolymerizing action on the siloxane chain. Mercurous oxide may however, react with the chain itself in some way. When mercurous oxide was added to a 20 volume GS199S recipe and cured for 24 hours at 400°F. it was found that the mercurous oxide increased hardness and modulus and decreased elongation with little effect on the tensile strength. A very slight improvement in compression set was obtained. It is concluded that the use of mercurous oxide is not worth while in GS199S Silica recipes in view of the poisonous properties of the chemical. The results are shown in Table II-C-5.

In several trials of softeners or plasticizers in GS199S Silica recipes it was found that little harmful effect on physical properties was obtained. Table II-C-6 shows the effect of three oils, paraffin, Circo and silicone oil, in a 25 volume recipe. It should be safe to use up to 5 per cent of any of these three plasticizers in GS199S Silica recipes.

TABLE II-C-4

EVALUATION OF VARIOUS GRADES OF TITANOX USING 15 VOLUME GS199S STOCKS

Compound No.	Titanox Grade	Stress @ 200%	Stress @ 400%	Tensile Strength p.s.i.	Elongation percent	Hardness Shore A
2095	LP-561-4	282	510	1010	700	52
2096	LP-561-5	306	495	710	562	68
2097	LP-561-6	296	574	675	475	50
2098	LP-561-8	285	538	778	537	61
2099	LP-561-9	269	487	780	625	57
2100	LP-561-10	316	600	910	575	61

Ten volume stocks of Titanox were used.
The stocks were compounded with SE-76 silicone gum (Batch No.5946)
The press cure was 15 minutes at 230°F.
The oven cure was 1 hour at 300°F. plus 18.5 hours at 400°F.

TABLE II-C-5

EVALUATION OF GS199S STOCKS CONTAINING MERCUROUS OXIDE WITH VARYING AMOUNTS OF BENZOYL PEROXIDE

Compound No.	Percent Benzoyl Peroxide	Stress @ 100%	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	Compression Set Percent	Cold Test at -90°F.
2132	None	395	729	300	73	67.9	Passed
2133	0.5	658	764	150	85	67.5	"
2134	1.0	---	650	63	86	61.0	"

The stocks were compounded with SE-76 silicone gum (Batch No.5946)
The press cure was 15 minutes at 230°F.
The oven cure was 24 hours at 400°F.
Twenty volume stock of GS199S were used.
1 percent Hg_2O was incorporated in each compound.

TABLE II-C-6

PLASTICITY STUDY OF 25 VOLUME GS199S STOCKS

Compound No.	Plasticizer	Percent Plasticizer	Stress @ 200%	Stress @ 400%	Tensile Strength p. s. i.	Elongation percent	Hardness Shore A
2170	None		250	450	1325	725	68
2166	Paraffin	1.0	268	535	1375	675	65
2166-1	Paraffin	2.0	279	522	1300	675	64
2166-2	Paraffin	3.0	255	497	1363	725	66
2166-3	Paraffin	5.0	242	458	1128	700	66
2167-1	Circo Oil	1.0	267	546	1463	725	66
2167-2	Circo Oil	3.0	248	455	1291	738	66
2167-3	Circo Oil	5.0	237	525	1325	750	65
2169	Silicone Oil 9981 LT-4	5.0	253	460	1315	825	67

Stocks were compounded with SE-76 silicone gum (Batch #5946)
Press cure was 15 minutes at 230°F.
Oven cure was 1 hour at 400°F.
No benzoyl peroxide was used as a curing agent.

D. Shelf Aging GS199S Silica Stocks

A large master batch was prepared containing 25 volumes of GS199S Silica. It was then exposed at 125°F. in the vicinity of a steam radiator, for 21 days with samples being removed periodically. The samples were remilled to establish whether the stock appeared to be setting up in storage and then cured and tested. No change in workability on the mill could be detected. The results are shown in Table II-D-1. There appears to be no consistent change in the properties of this 25 volume stock in 21 days at 125°F.

The same master batch aged for two months at room temperature (April and May) was then cured and tested without remilling. Except for a slight stiffening, which could have been reduced by remilling, the results were satisfactory.

TABLE II-D-1

EVALUATING SHELF AGING TESTS OF 25 VOLUME GS199S MASTER BATCH

Compound No.	Date of Remilling	Stress @ 200%	Stress @ 400%	Tensile Strength p.s.i.	Elongation percent	Hardness Shore A
1985-A (B1) (control)	4-9-52	179	274	1695	900	56
1985-A (B2)	4-14-52	170	234	1570	925	55
1985-A (B3)	4-17-52	160	254	1385	900	55
1985-A (B4)	4-21-52	171	282	1635	950	54
1985-A (B5)	4-23-52	190	288	1615	900	53
1985-A (B6)	4-25-52	189	295	1417	868	50
1985-A (B7)	4-28-52	184	296	1563	900	53
1985-A (B8)	4-30-52	178	288	1310	875	52
1985-A (A1)	Not remilled(aged 2 months)	217	371	1768	800	64

The stocks were compounded with SE-76 silicone gum(Batch #5946)
No benzoyl peroxide was used as a curing agent.
The press cure was 15 minutes at 230°F.
The master batch was heated continuously at 125°F. until date of remilling except 1985A(A1) which was aged 2 months at room temperature.
Oven cure was 1 hour at 400°F.

III. ANALYSIS OF GS199S SILICA AND PREPARATION OF SILICA PIGMENTS

A. General characteristics of GS199S Silica Pigment.

GS199S filler is a fine silica pigment manufactured by the Grasselli Chemical Division of Du Pont. It has an ultimate particle size of 0.01μ. It emits a very strong odor similar to that of some of the amyl alcohols and is extremely hydrophobic. It is quite organophilic, mixing easily with acetone, ethyl ether, petroleum ether and carbon tetrachloride.

When heated to 500°C it turns brown, frequently burns with pale flame and at high temperatures returns to a white color, losing about 11.8 per cent of its weight (the manufacturing company claims it has 15 per cent by weight of an organic coating). After burning, the hydrophobic properties of the filler disappear.

When the pigment is milled into G.E. SE-76 silicone gum, up to 55 volume per cent can be added. However, the heated pigment, which has lost its coating, does not mill into the gum in loadings of more than 10 volume per cent. This fact indicates that the organic coating is responsible for the exceptionally good dispersion of this filler in silicone gum.

GS199S exerts a curing action on silicone gum in the absence of benzoyl peroxide or any other curing agent above 10 volume loadings, giving very good physical properties to the gum. The heated pigment lacks this curing property.

The filler itself shows no unsaturation to bromine or potassium permanganate and does not give any positive peroxide reaction. When heated in a nitrogen stream at 105°C for 8 hours it loses 0.3 per cent by weight of water.

B. Analysis of GS199S filler

1. Extraction with organic solvents.

Various attempts to extract the organic coating from GS199S by means of organic solvents failed completely. Chloroform, ethyl ether and petroleum ether did not extract any appreciable amount of the coating even after prolonged contact and heating. The filler which had been extracted could be milled with no difficulty at the same volume loading used for non-extracted pigment. The inability of organic solvents to extract the organic coating existing on the surface of GS199S points to a chemical rather than physical bond between the surface of the silica and the coating.

2. Dry distillation of GS199S filler.

Following the findings reported above, it was apparent that stronger means were necessary to isolate the coating from the silica substrate. Therefore, large samples of GS199S were dry distilled at temperatures up to 400°C. at 10^{-3} mm. Hg for several hours, and the products of the distillation were collected in a trap cooled with dry ice. Beginning at about 80°C., a clear distillate was obtained, which froze in dry ice, evaporated easily at room temperature, and had a neutral pH; its boiling range was 86-96°C. This portion reacted with bromine and potassium permanganate, indicating it to be an unsaturated compound. Above 150°C. a yellowish oil was collected. This was not miscible with the first liquid, froze in dry ice and boiled between 105 and 117°C. Its specific gravity was 0.82 g/cc. This oil did not contain any nitrogen, sulfur or halogens. Benzoyl chloride reacted readily with the distillate in question, yielding white crystals of an ester (indication of alcoholic radical groups). Sodium metal reacted vigorously with the product, indicating the presence of hydroxyl groups. The oil reacted with bromine and potassium permanganate, indicating unsaturation, and infrared absorption spectra of this portion pointed to a primary alcohol with traces of ketones. When the temperature during the dry distillation was increased to 350°C, white crystals appeared just outside the furnace in small quantity. The appearance of so many components during the dry distillation of GS199S led us to believe that a thermally destructive reaction was taking place and that little information could be gathered from this method.

3. Effect of Heating on GS199S Silica.

In Section II of this Report, it was stated that silicone stocks compounded with GS199S filler becomes brittle when cured at 480°F. A possible explanation of this phenomenon would be that at such high temperature of oven cure, the organic coating, which might be responsible for the curing action, might exercise too great a cross-linking action. It was thought that, if the amount of coating present were reduced, the embrittling effect would be decreased also. Therefore, GS199S Silica was heated in air until a part of the coating was removed. The filler turned brownish, and. when compounded with silicone gum and cured at 480°F. in absence of benzoyl peroxide, gave very poorly cured stocks of low physical properties.

It was apparent that during atmospheric heating, the coating on GS199S Silica oxidized. This oxidized material did not exhibit the normal curing action. Therefore, samples of GS199S Silica were heated (6 hours at 300°F, 6 hours at 400°F, and 6 hours at 480°F.) in vacuo without oxidation with a total weight loss of 4.09 per cent. The pigment, thus treated, was compounded with silicone gum and cured at 480°F. in the absence of benzoyl peroxide and the physical properties of the cured stock were found to be similar to those obtained with the untreated GS199S. (See Table III-B-3).

This indicates that about one quarter of the organic coating may be removed from GS199S by heating at 480°F without impairing its curing action. The fact that most of the organic coating remains on the silica at 480°F is proof of the tight bonding of the alkoxy groups to the silica.

4. Extraction with sodium hydroxide.

Since silica is attacked by strong alkali, we tried dissolving the silica substrate of the GS199S pigment with aqueous sodium hydroxide and then extracting the coating from the aqueous solution with an organic solvent. Large samples of the pigment were dispersed in ethyl ether and shaken repeatedly with a 3 N aqueous solution of sodium hydroxide. The ether layer containing the organic

TABLE III-B-3

Effect of vacuum heated GS199S in G.E. SE-76 gum, batch 11317-5 15 volume loading
(Without benzoyl peroxide)

Compound No.	Oven cure	Weight loss of filler	Stress @ 200%	Tensile Strength psi	Elongation percent	Hardness Shore A
2351(A)	24 hours at 300°F.	4.09%	195	560	675	60
2311(A)	"	None	98	420	900	43
2351(B)	16 hours at 400°F.	4.09%	312	476	375	64
2327-1(A)	"	None	242	480	500	56
2351(C)	16 hours at 400°F. + 6 " " 480°F.	4.09%	--	312	100	72
2327-1(B)	"	None	--	410	100	71

Press cure: 15 minutes at 230°F.
Oven cures: as indicated

constituents was separated, dried over sodium sulfate, and finally carefully fractionated. Several portions were identified, with boiling points between 80 and 117.5°C. The high boiling portion constituted approximately 7 per cent by weight of the original pigment, and all identification work was based on this portion.

The physical properties of the constant boiling fraction were as follows: boiling point 116-117.5°C; n_D^{20}=1.398; sp.gr. $\frac{20}{4}$ =0.81. Nitrogen, sulfur and halogens were not present. The addition of sodium metal to a dry sample of the product caused vigorous reaction with evolution of a gas (indication of -OH groupings of alcohols of intermediate molecular weight) :

$$2ROH + 2Na \rightarrow 2RONa + H_2$$

The addition of dry ether to the mixture precipitated the white sodium salt of an alcohol.

Iodic acid reacted positively with liberation of free iodine:

$$3RCH_2OH + HIO_3 \dashrightarrow 3RCOOH + 3HOH + 2HI$$

$$5HI + HIO_3 \dashrightarrow 3I_2 + 3HOH$$

An attempt to prepare the alkyl halide of an alcohol by means of a hydrochloric acid-zinc chloride mixture failed (primary alcohols of low molecular weights do not react readily).

A derivative from 3,5 dinitro benzoyl chloride (3,5 dinitroalkyl benzoate) was prepared, melting point 65°C.

$$(NO_2)_2C_6H_3COCl + HOR \longrightarrow (NO_2)_2C_6H_3COOR + HCl.$$

A urethan derivative was made from phenylisocyanate, melting point 58-59°C.

$$C_6H_5N{=}C{=}O + HOR \longrightarrow C_6H_5NHCOOR$$

This derivative was analyzed by the Microchemical Laboratory of the Massachusetts Institute of Technology, Cambridge, Mass. with the following results:

Calcd. for butyl urethan: C,68.36 ; H,7.82;O,16.55 ; N,7.25
found: C,68.08 ; H,7.84;(O),16.66; N,7.42

Infrared absorption spectra of the product boiling at 116-117.5°C corresponded exactly with the spectra obtained from pure n-butyl alcohol.

5. Comparison of results of our analysis and properties of n-butanol

Product from GS199S	n-Butanol
b.p.116-117.5°C	b.p.117.7°C
n_D^{20}=1.398	n_D^{20}=1.399
sp.gr.$\frac{20}{4}$=0.81	sp.gr.$\frac{20}{4}$=0.8097
benzoate,m.p. 65°C	benzoate,m.p. 64°C
urethan,m.p. 58-59°C	urethan,m.p. 57°C

From these data and from the infrared spectra it was concluded that the product obtained by treating GS199S filler with strong alkaline solutions was n-butanol (7-8 per cent by weight of the original pigment), probably attached chemically to the silica in the form of butoxy groups which may be hydrolyzed off to give the corresponding alcohol.

C. <u>Preparation of alkoxy-substituted silica pigments</u>.

Because of our interest in the GS199S self-curing coated silica pigment, we have conducted a few experiments to prepare a similar silica pigment with an organic constituent attached.

<u>1. Hydrolysis and Condensation of alkyl chlorosilanes</u>

It seemed possible that a pigment which contained a number of alkyl groups attached to the silica structure would exhibit a curing action through fission of the alkyl groups from the silica substrate by heat with consequent formation of alkyl free radicals. Therefore methyl and ethyl trichlorosilanes were hydrolyzed with water and allowed to condense to a whitish powdery solid. When samples of these powders were heated over a free flame they turned brown and caught fire, indicating that an organic constituent was present. Amyl trichlorosilane was also hydrolyzed by the same method but a solid product was obtained only when it was hydrolyzed together with silicon tetrachloride. None of the above mentioned alkyl substituted silicas exhibited appreciable curing action when compounded into silicone elastomer alone. With 2 per cent benzoyl peroxide, the methyl and ethyl substituted pigments gave no reinforcement but the condensation product of amyl trichlorosilane and silicon tetrachloride exhibited a slight reinforcing action. (Elongation: 600 per cent, hardness: 10, tensile: 54).

2. Hydrolysis and Condensation of tetraethylortho silicate.

The next experiment was to hydrolize partially tetraethylortho silicate in such a way that ohly a fraction of the number of the original ethoxy groups would be present in the final product and the silicate would condense to form a silica like structure. A calculated amount of water was added to a solution of tetraethylorthosilicate in isopropanol, a small amount of hydrochloric acid added to accelerate the hydrolysis and the mixture was poured into aqueous sodium hydroxide. A transparent gel was obtained which, after repeated washings and after drying, converted into a white powder. Here again, when this silica-like powder was compounded with silicone elastomers in the absence of benzoyl peroxide, no cure was obtained. In one case the addition of

2 per cent benzoyl peroxide caused some reinforcement (tensile: 96, elongation: 450 per cent, hardness: 15).

3. Alkoxy substituted silica pigments

Results of our analysis of the GS199S pigment caused us to suspect that the n-butanol obtained by hydrolysis of the pigment was attached to the silica through ester-like bridges. Therefore, the coating itself is constituted of butoxy groups on the surface of a silica gel structure.

The patent literature has reported successful substitution of alkoxy groups on halogen substituted silicone polymers (M.Sveda,U.S.2,561,429 and 2,562,000) using a tertiary amine to neutralize the hydrogen chloride evolved during the reaction.

Our idea was to hydrolize partially silicon tetrachloride with water in such a manner as to leave an average of one chlorine atom untouched, and then to react the latter with n-butanol through alcoholysis. The silicic acid formed in hydrolysis by water should condense to form a silica gel structure. In the cases reported in the patent literature, hydrolysis of the halogen groups by means of alcohol radicals could go to completion without fear of overextending the reaction. However, in our case it was possible that all the chlorine atoms of silicon tetrachloride could be hydrolyzed, not only by water introduced into the system, but also by the water formed by the condensation of the silicic acid. Therefore, after several experiments, we decided to use a minimum amount of water to initiate the hydrolysis and to count on the water split off during the condensation to continue hydrolysis to the desired extent. Alcohol was then added to complete the reaction and to introduce the desired alkoxy groups.

Dry ethyl ether was used as diluting agent and two methods were followed:

a. Silicon tetrachloride dissolved in ether was added slowly to a rapidly stirred mixture of water and ether at approximately 0°C. Then an excess of n-butanol was added to complete alcoholysis.

b. (See W.C.Schumb, A.J.Stevens, J.A.C.S.72, 3178(1950). Water was added to silicon tetrachloride dissolved in ether at a temperature of -10 to -20°C. with rapid stirring, then a slight excess of n-butanol was added. This second method seemed to give more reproducible results. The addition of molar quantities of pyridine to neutralize the hydrochloric acid given off during the reaction did not improve the results appreciably and, therefore, no amine was used in our experiments. An example of the manner in which an alkoxy-substituted silica was obtained is the following:

To 100 grams of silicon tetrachloride (0.587 moles) in 130 cc. of anhydrous ether, was added very slowly 10.6 grams (0.587 moles) of water over a period of 1/2 hour, keeping the temperature between -10 and -20°C. by means of a dry-ice bath, and with continuous rapid mechanical stirring. The reaction took place with evolution of hydrochloric acid vapors. The mixture was stirred 10 minutes longer in the ice bath, and was allowed to stand 1/2 hour. The color of the solution was orange-pink. Then 64.4 grams (0.86 moles) of n-butanol was added dropwise (1 drop per second) with the temperature in the reaction vessel being between -20 and -40°C. At the end of addition, the dry-ice bath was removed and the mixture was stirred at room temperature for 1/2 hour, then heated for 2 hours at 35-40°C. Condensation of the resulting product was slow, but it was aided by heating and washing with a very dilute aqueous solution of ammonium hydroxide. The resulting solid could be ground to a fine mesh, and was compounded with silicone polymers. This pigment had a surface area of 121 sq. meters per gm. (by N_2 absorption) which indicates an average particle size of 0.03 micron or larger if the particles are porous.

By the above mentioned method pigments could be made whose butoxy coatings varied from 5 to 55 per cent. When exposed to an open flame these pigments acted similarly to GS199S, burning with pale flame, emitting acrid odors, blackening considerably and then returning to white. They were hydrophobic and organophilic; treatment with alkali hydrolyzed the coating off (n-butanol was identified as the main product of hydrolysis). Samples which contained about 30 per cent by weight of butoxy groups were found to give a slight but definite curing action when compounded with SE-76 and heated to 400-480°F.

This work substantiates our belief that a large portion of the organic coating of GS199S is butoxy, and that this system will act as a curing as well as reinforcing agent for silicone elastomers.

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